TREATMENT OF CHROMIUM CONTAMINATED SOIL BY CO-PYROLYSIS WITH RICE STRAW

by

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Abstract

The direct discharge of tannery waste and effluent could result in severe chromium (Cr) contamination in soils. This study focused on the remediation of Cr-contaminated soil via co-pyrolysis with rice straw. The influence of co-pyrolysis temperature, rice straw / soil mixing ratio and reaction time on Cr immobilization were investigated. Compared to untreated soil, the leachable Cr and total Cr(VI) in co-pyrolyzed soil were decreased by up to 95 % and 86 %, respectively. With increasing temperature and rice straw addition, the leachable Cr and total Cr(VI) were reduced. Reaction time did not show a significant effect on Cr immobilization. The time-varying desorption test indicated that the equilibrium amount of released Cr in various extractants was inhibited by co-pyrolysis. The Simple Bioaccessibility Extraction Test also showed that the bioaccessible Cr in the gastric phase was decreased after co-pyrolysis. The results suggested that co-pyrolysis was beneficial on Cr immobilization.

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Glossary

ANOVA	Analysis of variance
BET	Brunauer–Emmett–Teller
CCME	Canadian Council of Ministers of the Environment
CEC	Cation exchange capacity
COPR	Chromite-ore-processing residue
CRP	Cr(VI) reduction percentage
EDTA	Ethylenediaminetetraacetic acid
FAAS	Flame atomic absorption spectrometer
FTIR	Fourier-transform infrared
LOI	Loss-on-ignition
LSD	Least significant difference
nZVI	Nano zero-valent iron
PBET	Physiologically based extraction test
pH_{PZC}	pH of point of zero charge
RBALP	Relative bioaccessibility leaching procedure
SBET	Simple bioaccessibility extraction test
SEM	Scanning electron microscopy
SPLP	Synthetic precipitation leaching procedure
TCLP	Toxicity characteristic leaching procedure
US EPA	United States Environmental Protection Agency
XRD	X-ray diffraction

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Chapter 1 Introduction

The sharp development in industrial activities, such as leather tanning, contributes to enormous effluent and sludge waste with high concentrations of heavy metals. The disposal of these effluents and sludge wastes without rigorous treatment causes soil contamination and poses a severe threat to human health. China, as one of the biggest leather-producing countries in the world, generates a high amount of pollution during the leather manufacturing process annually (Dang and Shan, 2018). For example, sludge and wastewater discharged from leather plants in Shuitou Town, Pingyang, China have contaminated the nearby alluvial soils with chromium (Cr). Since the waste was not previously proper treated before discharge, the Cr concentration was found to be as high as 2484 mg kg^{-1} in the soil (Chen et al., 2012).

Cr as one of the hazardous heavy metals cannot be destroyed by chemical degradation or biodegradation, but remains and accumulates in the soil leading to biomagnifications (Mishra, 2017). However, Cr contaminants are still largely generated and increase in total amount due to rapid and continuing economic development (Liikanen et al., 2018). Cr-contaminated soil may present a unique set of problems due to the complex chemistry of Cr. There are many oxidation states of Cr, ranging from Cr^{2+} to Cr^{6+}. The most common and stable forms in the soil are Cr(III) and Cr(VI) species. These two species have different chemical properties, and their influence on organisms are different. Cr(VI) is water soluble in the full pH range, and it is highly toxic to all forms of living organisms and may cause death of animals and humans when ingested in large doses (Zayed et al., 2003). Conversely, Cr(III) is relatively immobile as it has strong adsorption capacity to negative charged ions and colloids in soil, and subsequently precipitates in the form of $Cr(OH)_3$ in the pH range 4–8 (Dhal et al., 2013). The most mobile forms of Cr(VI) found in the soil are CrO_4^{2-} and $HCrO_4^-$, which are easy to diffuse across the cell membrane, but the low solubility of Cr(III)

makes it difficult to penetrate cellular membranes (Shahid et al., 2017; Dhal et al., 2013). Therefore, the treatment to reduce the toxicity of Cr-contaminated soil is thought to be a matter of great concern.

In order to reduce the toxic of Cr in the soil, two main approaches can be applied, i.e., removing Cr from the soil or immobilizing it. Traditional methods such as chemical treatment, bioremediation and phytoremediation have their own advantages and drawbacks. For example, chemical treatment is a simple and fast remediation method, but it needs high cost and may cause secondary pollution at contaminated sites (Yao et al., 2012). There remains an urgent demand to explore an appropriate technology to reduce the toxicity of Cr-contaminated soil. Research is therefore focused on the pyrolysis technology that can meet environmental challenges. Pyrolysis is an effective and relatively cost-saving thermal treatment to inhibit heavy metal release and reduce Cr(VI) to less toxic Cr(III) (Xu et al., 2008; Swarnalatha et al., 2006). Zhang et al. (2009) explored the influence of pyrolysis on Cr, Zn, Pb, Cu, Hg and Cd in sediment, and the results showed pyrolysis strongly immobilized metals and transformed Cr(VI) to less soluble Cr(III). Taking into account the high concentration of Cr in the soil contaminated by leather tanneries, a more effective and stable method is essential for practical application to minimize the environmental risk. This may be achieved by using some additives to enhance the efficiency of immobilization of Cr during pyrolysis treatment.

Rice production is common worldwide, generating a large amount of rice straw. The biochar from rice straw has strong adsorption capacity due to its large surface area and microporosity (Jiang et al., 2012). Furthermore, rice straw consists of cellulose, hemicellulose, and lignin. During the pyrolysis, the release of volatile organic matter can form a reduction atmosphere, which is beneficial for converting Cr (VI) to Cr (III) (Zhang et

al., 2016). By-products of pyrolyzed cellulose including catechol, diols and other compounds can perform as reducing and chelating agents toward metal ions (Mohan et al., 2011). These characteristics of rice straw indicate that it may be an effective and environmentally-friendly additive to help immobilize Cr. Hence, rice straw is selected as a cost-effective additive in the present study to be co-pyrolyzed with Cr-contaminated soil for achieving Cr immobilization.

In the present study, the co-pyrolysis treatment of Cr contaminated soil with rice straw at different temperatures (100-300℃) was explored to immobilize Cr in the contaminated soil using a bench-scale apparatus. The influence of co-pyrolysis parameters, including temperature, mixing ratio of rice straw to soil and reaction time, on the leaching of Cr and Cr (VI) reduction behavior was investigated. The main objectives of the study were: (1) to analyze the characteristic changes of soil before and after co-pyrolysis treatment; (2) to evaluate the reduction of Cr (VI), stability and leachability of Cr in the co-pyrolyzed samples; (3) to find the optimal parameters of co-pyrolysis application to efficiently immobilize Cr in the soil; This thesis can advance the understanding of characteristics of co-pyrolyzed chars produced by mixing Cr-contaminated soil with rice straw. In recent years, some efforts have been made to explore the products of co-pyrolysis of sewage sludge and different kind of biomass (Jin et al., 2017; Huang et al., 2017). However, only a few reports studied the application of co-pyrolysis to Cr-contaminated soil and the impacts of co-pyrolysis on the behavior of Cr under temperature100-300 ℃. It should be noted that lower temperature co-pyrolysis treatment not only saves energy and costs, but also helps reduce the more-toxic forms of Cr in the contaminated soil in an easy and economic method.

Chapter 2 Literature Review

2.1 Chromium contamination in the soil

Chromium is regarded as a vital contaminant released into the environment by many industrial activities (Mishra and Bharagava, 2016). Unlike organic contaminants, chromium in the soil environment can not be destroyed by chemical degradation or biodegradation, but remain in soils causing biomagnifications. They would also accumulate in the food chain, which contributes to a significant threat to public health and safety (Mishra, 2017). Recently, Cr contamination in soil was frequently reported in the world (Ballesteros et al., 2017; Li et al., 2012; Khan, 2001), and Cr discharges into the environment were found to far exceed the international guidelines values (50-100 kg per year) (Gil-Cardeza et al., 2014). It was reported that approximately 200,000 tonnes of chromite ore processing residue (COPR) was deposited in Xiangxiang, Hunan, China, and the soil collected in this area contained 19,700 mg kg^{-1} Cr (III) and 5,880 mg kg^{-1} Cr (VI) (Xu et al., 2011).It has also been reported that the maximum concentration of Cr in the soil is around 64 mg·kg^{-1} to protect environment and human health (CCME, 2015). Therefore, the treatment and disposal of soils polluted by the use of this metal has attracted increasing attention (Donkor et al., 2005).

Many industrial activities such as steel production, wood preservation, mining, ink manufacture, electroplating and leather tanning can cause elevated levels of Cr content, because generated Cr waste can be spread in the soil (Viti et al., 2003). In addition, some agriculture practices, such as the use of sewage sludge from leather tanning containing high concentration of Cr, are responsible for the stream of this metal into the biosphere (Ertani et al., 2017). During leather processing, the putrescible skin has to be converted into imputrescible leather with tanning agents, among which chromium sulfate is the most

popular reagent (Nashy et al., 2011). The excess chromium salts not being used will be charged into the effluents. Besides, organic fertilizers, such as phosphorus fertilizers and biosolids containing large amounts of Cr, are considered as a source of Cr pollution in agricultural soils (Vogel et al., 2015). Although Cr is still a kind of fundamental micro-nutrient in the diet of animals and humans because of its effect to mammals' normal sugar, lipid and protein metabolism, high levels of Cr is still toxic even in its oxidation state (Sharma et al., 2011).

2.2 Chemistry of chromium

Chromium, as a naturally occurring element, is the 7th most abundant element in the Earth and the 21st on the Earth's crust (Dhal et al., 2013). Furthermore, Chromium has a complex electronic and valence shell chemistry, because it can easily transfer from one oxidation state to another (Prado et al., 2016). Inorganic chromium compounds occur in valence states ranging from -2 to +6, but the most common and stable forms in the soil are Cr(III) and Cr(VI) species (Ashraf et al., 2017), owing to their predominance and stability in the ambient environment. These two species have different chemical properties, and their influence on organisms are different. Normally, Cr (VI) mainly occurs in the form as oxyanions such as hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$) and chromate (CrO_4^{2-}) ions (Mandina and Mugadza, 2014). Cr (VI) is water soluble in the full pH range, and it can be reduced to Cr (III) in the presence of organic matter (EPA 1984). Conversely, Cr (III) is considered an essential micro-nutrient at relatively low levels for human and animal health (Eskin, 2016), largely because it is necessary for lipid and sugar metabolism (Bai et al., 2015). It is also relatively immobile as it has strong adsorption capacity to negative charged ions and colloids in soils, and subsequently precipitates in the form of $Cr(OH)_3$ in the pH range 4–8

(Dhal et al., 2013). As the pH decreases, it is scarcely mobile and present in insoluble inorganic compounds (Dhal et al., 2013).

The two main species of Cr can interchange and coexist in the chromium cycle (Figure 2.1), which is a dynamic balance predominantly regulated by oxidation and reduction. Cr (VI) is a strong oxidizing agent, and it can be easily reduced to Cr (III) in the presence of organic matter under acidic conditions. On the contrary, Cr (III) in the soil can be oxidized by manganese oxide (MnO_2) through surface oxidation under neutral pH (Apte et al., 2005). It has also been reported that oxidized Cr (III) amount is proportional to the Mn oxide contents and to the reduced amount of MnO_2 (Ertani et al., 2017). Although organic matter and divalent iron can accelerate the reduction of Cr (VI) to a rather stable form Cr (III), high concentration of Cr (VI) can impede this reduction (Cervantes et al., 2001). Besides, Cr (VI) is preferred to be adsorbed by the positive charges on the mineral coating of iron oxides with the releasing of OH^- groups (Stollenwerk and Grove 1985). Moreover, soil redox potential (Eh) and pH also play important roles in the speciation of Cr. Normally, reduction process is present at low Eh, and will increase pH by consuming protons while oxidation is the opposite (Shaheen and Rinklebe, 2014; Frohne et al., 2015). Soil pH can greatly affect sorption/desorption processes and speciation of Cr (Amin and Kassem, 2012). Cr (III) has low solubility at $pH < 5.5$, and will completely precipitate and be stable in the soil at $pH > 5.5$ (Kabata-Pendias, 2010). Otherwise, Cr (VI) remains unstable and mobilized in both acidic and alkaline soil pH (Kabata-Pendias, 2010).

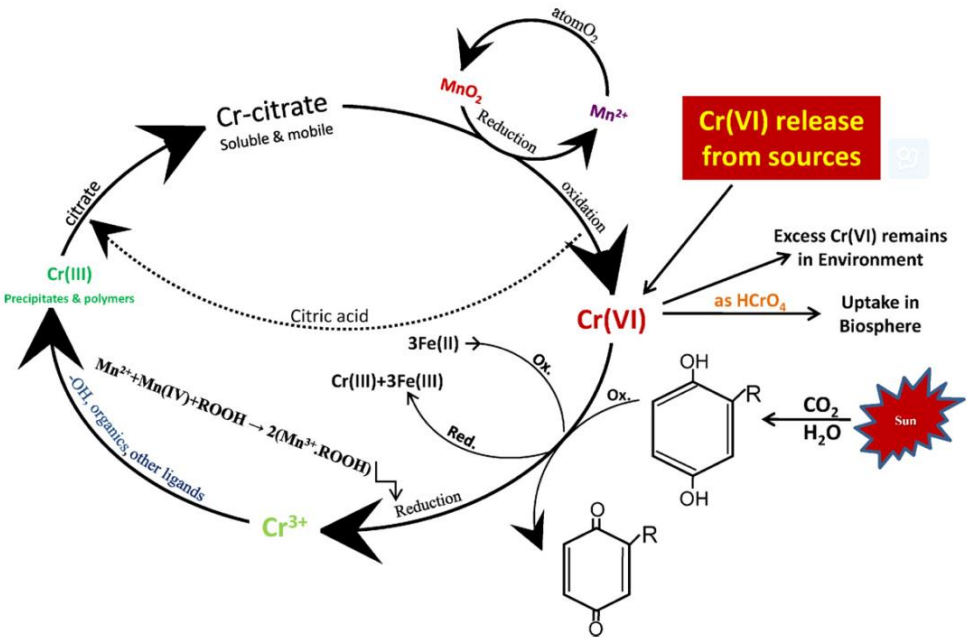


Figure 2.1 The natural chromium cycle in the environment (Dhal et al., 2013)

2.3 The toxicity of Cr

Although Cr is an essential nutrient for humans and mammals, it is still listed as one of the priority 129 environmental contaminants by the Environmental Protection Agency (Sharma et al., 2012). Moreover, Cr(VI) is regarded as one of the 14 most toxic elements for the health of living organisms (USEPA 2000). The positive or negative effects depend on the dose, exposure time, and its oxidation state (Ertani et al., 2017). Humans and mammals can be exposed to Cr by ingestion, skin contact and inhalation (Ertani et al., 2017). Chromium uptake by vegetables and accumulation in edible plant parts can induce health problems to consumers (Noli and Tsamos, 2016), and the consumption of these is the major pathway for humans to exposure to Cr other than skin contact and breathing (Wang et al., 2011; Xiong et al., 2014).

Cr (III) is considered as a kind of nutrient for humans and mammals when the daily intake dose is between 50 and 200 μg day^{-1}, because it can participate in glucose metabolism,

decrease the body fat, cholesterol and triglyceride levels, activate enzyme reactions, and increase the muscle mass (Bielicka et al., 2005). However, people whose daily intake of Cr(III) is higher than this criterion will also experience health problems. Compared to Cr(III), Cr(VI) is 10–100 times more toxic to all forms of living organisms, and may cause death of animals and human when ingested in large doses (Zayed et al., 2003). The LD50 (dose that causes the death of 50% of a defined animal population) of oral toxicity for rats is 50 – 100 mg kg^{-1} for Cr(VI) and 1900–3000 mg $kg^{-1}$for Cr(III), indicating that Cr(VI) is more toxic than Cr(III) (Shahid et al., 2017). The main mechanism of Cr(VI) toxicity is related to its easy diffusion across cell membranes, followed by the reduction of Cr(VI) in cells producing free radicals (OH·, O, $O2^{-}$, RS·, R·) which finally cause DNA alterations (Kotasâ & Stasicka, 2000). In addition, the reduction of Cr (VI) will generate unstable Cr intermediate species (Cr(IV) and Cr(V)), which will produce more free radicals during the reduction process (Costa, 2003). Alternatively, the excess of Cr (III) is less toxic, because most Cr (III) is unlikely to penetrate cellular membranes (Shahid et al., 2017). Chromium is required in trace amounts for mammals, but it is not an essential element for plants (Lukina et al., 2016). A few studies reported that relatively little amount of Cr may promote the productivity of plants (Prasad et al., 2010), but it has also been shown that exposure to Cr may bring some toxic effects in several biochemical processes, including plant germination, root growth and length, stem growth and leaf development (Tiwari et al., 2009).

2.4 General remediation techniques of Cr contaminated soil

Many technologies exist for the remediation of heavy metal contaminated soil, such as isolation and containment, phytoremediation, chemical treatment, bioremediation and pyrolysis treatments.

2.4.1 Isolation and containment

Isolation technologies can prevent the movement of contaminants by isolating and containing them within a certain area, which can reduce the available pollution by reducing the exposed area or leachable contaminants. According to the requirement of US EPA, it is required to reduce the permeability of waste to less than 1×10^{-7}m/s (USEPA, 1994). It is aimed at separating the contamination temporarily, and is usually implemented during the site assessment and remediation. Physical walls include vertical and horizontal barriers. Vertical barriers are mainly used for groundwater treatment. They can help reduce the transfer of polluted groundwater and separate the unpolluted groundwater from polluted groundwater (Jankaite and Vasarevičius, 2005). On the contrary, technologies for the construction of horizontal barriers are still under development. Horizontal barriers have the potential to control the downward movement of pollutants through using liners without excavation of the contaminated site. Therefore, the isolation technology can limit the contacting of potential existing contamination and its source by human, fauna, and flora (Dermont et al., 2008). However, the toxicity of the polluted site is not reduced, and it does not involve the treatment of the soil (Martin et al., 2004). Furthermore, the long-term effect of this treatment has not yet been proven, and monitoring systems may also be required.

2.4.2 Phytoremediation

Phytoremediation technology is defined as the use of plants to remove, destroy or sequester contaminants from the environment (Jankaite and Vasarevičius, 2005). There are five main subgroups of phytoremediation: phytoextraction, phytodegradation, rhizofiltration, phytostabilisation, and phytovolatilization. First, this technology was being driven by the high cost of other remediation approaches, and using metal-accumulating plants to remediate

soil and water is a sustainable and environmental friendly technology. Furthermore, phytoremediation can prevent erosion of soils and leaching of contaminants (Paz-Ferreiro et al., 2014). However, the plants used must have the certain hyperaccumulation ability, and they can accumulate heavy metals at a level 100 times greater than common plants without yield reduction (Chaney et al., 2007). In addition, these plants must not only accumulate high levels of heavy metals but also have high growth rates, strong adaptability to the local environment, strong resistance to pathogens and be easy to be cultivate (Ali et al., 2013). After accumulating certain concentrations of heavy metals, these heavy metals will be removed through harvesting of the plants and burning them.

Phytoremediation can also be achieved by changing the speciation of heavy metals to decrease their bioavailability and toxicity (Rahman et al., 2016). Some researchers have investigated the use of phytoremediation to reduce the toxicity of Cr in the soil. Kumpiene et al., (2008) found that two elements, Cr and Pb, can be immobilized by a vegetation cover, which is cost-effective and environmentally sustainable. In addition, deep rooted plants are found that could effectively reduce the highly toxic Cr (VI) to less toxic and less bioavailable Cr (III) (Pulford and Watson, 2003). Furthermore, it is known that Cr can not be easily transferred to above-ground plant tissues, predominantly being held in the roots (Pulford et al., 2001). Singh and Sinha, (2004) reported three aquatic plants (*Scirpus lacustris, Phragmites karka* and *Bacopa monnieri*) grown on tannery sludge to assess the ability of them to absorb, translocate and concentrate metals under different chromium concentrations. The results showed that these three plants were able to grow in tannery sludge containing 214 mg kg^{-1} Cr and reduce the concentration of Cr significantly with an increase in the plant's biomass. Paisio et al., (2018) suggested that *Lemna minuta Kunth* was also as a suitable

candidate for the phytoremediation to remove Cr (VI) and phenol, and it can grow normally without damage on photosynthetic processes.

It is recognized that phytoremediation can improve the chemical and biological characteristics of contaminated soil, like increasing organic matter, nutrient amounts, cation exchange capacity (CEC) and biological activity (Arienzo et al. 2004). Furthermore, phytoremediation can efficiently prevent landscape destruction and develop the diversity of soil microorganisms to maintain a healthy ecosystem (Vamerali et al., 2010). Compared to other remediation methods, phytoremediation is more economical and less disruptive to the environment. Excavation and transportation of pollution to the disposal sites can also be avoided, which is easily accepted socially by the public. Although this technique is effective in remediating heavy metal contaminated soils, these still exist many problems during the application process. Sutton and Dick, (1987) found that the main constraint of establishing vegetation cover is the acidity of the soil, although organic residues, liming materials and lime-stabilized biosolids can help weaken the effects of soil acidity (Basta et al. 2001). Besides, only a narrow range of species can grow in heavy metal rich soil (Peng et al., 2006). There are several other challenges in practice due to the lack of information on the agricultural management of these hyperaccumulators, slow-growing and poor shoots and roots (Navari-Izzo and Quartacci 2001; Mitch 2002). Moreover, phytoremediation may be an inappropriate method to remediate sites where the heavy metal concentration is too high because phytotoxic symptoms can occur in the plants (Paz-Ferreiro et al., 2014).

2.4.3 Chemical remediation

Chemical remediation use chemicals like sulfur dioxide, lime, ferrous sulfate and sodium sulfite to detoxify or decrease the mobility of heavy metals ((Jacobs et al., 2001). The

three reactions that can be used for this purpose are oxidation, reduction and neutralization reactions. The oxidation reaction changes the oxidation state of the metal atom through the loss of electrons. Many oxidizing agents are used to detoxify the precipitates or solubilize metals, including potassium permanganate, hydrogen peroxide, hypochlorite and chlorine gas (Mulligan et al., 2001). The opposite, reduction reaction is a process that changes the oxidation state of metals through adding electrons; the reduction agents are mainly alkali metals such as sulfur dioxide, sulfite salts and ferrous sulfate. Recently, a reducing agent, zero valent iron, has been widely used for chemical remediation of Cr contaminated soils (Fu et al., 2017). Neutralization reaction is usually implemented to adjust the pH of acidic or basic soils. It can also be used to precipitate insoluble metal salts in contaminated water or as a pre-treatment for oxidation or reduction reactions (Mulligan et al., 2001).

According to the literature, chemical treatment is often used to reduce Cr (VI) to Cr (III). Li et al., (2017) found that carboxymethyl cellulose (CMC) stabilized microscale iron sulfide (FeS) particles can effectively immobilize Cr (VI) in the soil. The total Cr and Cr (VI) in Toxicity Characteristic Leaching Procedure (TCLP) leachate decreased significantly, and the exchangeable Cr fraction was mainly converted to an Fe-Mn oxides bound fraction due to the precipitation of Cr(III)-Fe(III) hydroxides (Li et al., 2017). The possible mechanism of Cr (VI) reduction by FeS may be partial dissolution of Fe^{2+} and S^{2-}, which donate electrons to Cr (VI) (Mullet et al., 2004). Compared to iron sulfide, nanon-scale zero-valent iron is more frequently used for Cr (VI) removal. Di Palma et al., (2015) assessed the effectiveness of Cr (VI) removal from Cr contaminated soil using iron sulphate ($FeSO_4$) and colloidal nano zero-valent iron (nZVI). The results showed that both reducing agents could reduce Cr (VI) to Cr (III), but the reaction was faster and more efficient when colloidal nZVI was applied. They

also reported the reduction reaction leading to an increase of chromium in the oxide-hydroxide fraction and confirmed the mechanism of chromium-iron hydroxides precipitation.

Chemical treatment can be applied in-situ or ex-situ. In-situ chemical treatment is simple and fast, but it still has complex operations, high cost and will produce other contaminants in contaminated sites (Wuana and Okieimen, 2011). The continual use of reductants will produce much metallic sludge, and then this application will become ineffective or not cost-benefit. Therefore, chemical agents should be carefully selected when it applied for in-situ remediation to avoid secondary pollution. Sometimes, chemical treatment is not specific, and other metals may convert into more toxic or mobile forms.

2.4.4 Bioremediation

Bioremediation techniques involved the application of suitable living microorganisms to transform harmful pollutants into nontoxic compounds (Asha and Sandeep, 2013). Since heavy metals cannot be biologically degraded, sorption, uptake, precipitation and valence state charges are the main mechanisms to bioremediate metal contaminated soils. Microorganisms are known to oxidize and reduce heavy metal pollutants. For example, *Bacillus subtilis* and sulfate reducing bacteria in the presence of sulfur can transform Cr (VI) to less mobile Cr (III) (Mulligan et al., 2001). In addition, bioremediation is another technique that can bring contaminated site back to its original condition without any harmful impacts (Adhikari et al., 2004). Many living organisms like bacteria, fungi, yeast, algae are reported for their remediation capabilities. Although many microorganisms have been applied in many different research work and field remediation, the viability and metabolic activity of cells are still the main problems affecting the efficiency of detoxification (Cheung et al., 2007).

It has been reported that reductases like ChrR (from *Pseudomonas putida*), YieF (from *E. coli*) and Tkw3 (from *B. megaterium*) can transform Cr (VI) to Cr (III) through electron shuttle (Qamar et al., 2011). Thatoi et al., (2017) reported that Chromate transporters were responsible for Cr (VI) resistance, and it was identified by cloning and sequencing of the ChrA genes. The ChrA genes encode hydrophobic proteins (ChrA) of 416 and 401 amino acid residues in Pseudomonas aeruginosa and Cupriavidus metallidurans, respectively. After that, a 13-transmembrane segment, which is formed by the duplication of a 6-transmembrane segment ancestral protein, was found in ChrA in Pseudomonas, and these two half ChrA can achieve different functions in the Cr (VI) transformation (Cervantes and Campos-García, 2007). Ahemad, (2014) reported that the chromate tolerance of ChrA protein was related to the decreased accumulation of CrO_4^{2-}, and ChrA was assumed to involved in the extrusion of chromate ions. He et al., (2011) found a YieF gene and several genes which encode reductases were involved in chromate reduction. Das et al., (2014) isolated a Cr (VI) tolerant bacteria which was identified as *B. amyloliquefaciens and* found it could reduce 100 mg L^{-1} of Cr (VI) within 45 h when pH was 7 and temperature was 35 ℃ .

It is generally accepted by the public that engineered microorganisms are a better choice to reduce the toxicity of heavy metals, but their release is still a concern. The purified enzymes are frequently used in laboratory research, which can avoid culture sensitivity to ambient toxicants, but they are too expensive to be applied in field remediation. Sometimes, many polluted sites are lacking nutrients which may lead to a slow growth of bacteria, and the bioremediation efficiency is inhibited. A number of organic contaminants like petroleum hydrocarbons, alcohols and solvents can be biodegraded, but many industrial chemicals like PCBs and chlorinated solvents cannot be easily degraded (Boopathy, 2000). Different waste

sites have own circumstances and different contaminations, so bioremediation have to modified to adapt to each contaminated site.

2.4.5 Pyrolysis treatment

Pyrolysis is a kind of thermal treatment of organic compounds carried out in an oxygen-limited environment, which helps reduce metal leaching from several organic wastes such as sewage sludge (Méndez, et al., 2012), fly ash (Nowak et al. 2013), and biomass (Stals et al. 2010). During pyrolysis, many complicated reactions occur simultaneously, like dehydration, isomerization, depolymerization, decarboxylation, aromatization and charring (Collard and Blin, 2014; Lange, 2007; Vamvuka, 2011). It has been shown by many researches that the first step of pyrolysis is the evaporation of free moisture, and then oil cracking and repolymerization can occurr after the decomposition stage (White et al., 2011). Traditional methods such as incineration can help accelerate biomass energy recovery, but it is cost prohibitive and some toxic metals such as Pb and Cd may volatilize into the air or be retained in the fly ash, which needs further treatment (Nzihou and Stanmore, 2013). Compared to incineration, pyrolysis is a relative cost-saving technique which can make use of the energy generated from the combustion of the pyrolyzed biogas and maintain it without extra energy input (Hossain et al., 2010). Hence, pyrolysis presents many advantages, such as decreased amount of flue gas, repressed generation of acidic gases and dioxins, less pathogens, reduced bioavailability of heavy metals, especially Cr, and also transform organic materials to bio-energy. Research is therefore focused more on pyrolysis treatment (Erdem and Özverdi, 2008).

Research was conducted to explore the influence of direct application of pyrolysis to immobilize heavy metals in contaminated soils, and the results showed that this method did

have the potential to encapsulate some heavy metals (Pb, Cd) in contaminated soil by heat treatment (Debela et al., 2012). Zhang et al., (2009) examined the influence of pyrolysis treatment on the behavior of Hg, Cr, Zn, Pb, Cu and Cd in a sediment, and found that metals were strongly fixed in the treated sediment. It was also found that heavy metals would be transformed to more stable fractions after pyrolysis, and Cr (VI) could be efficiently reduced to Cr (III). Devi & Saroha, (2014) also observed that heavy metals became enriched in biochar matrix after pyrolysis, but the bio-available heavy metals in biochar were immobilized. The resultant biochar was analyzed by sequential extraction procedure to assess the mobility, bioavailability and leaching potential of heavy metals in the biochar. The results showed that pyrolysis could convert heavy metals from unstable fractions (F1, F2, F3 and F4) into non-bioavailable fraction (F5) which was not prone to leaching and degradation. There are two reasons to explain the immobilization of heavy metals by pyrolysis. One is that metals can react with SiO_2 and Al_2O_3 in the mineral phase at a high temperature (Jin et al., 2009). Another reason is that high pH during pyrolysis can decrease the dissolution of metals (Zhang et al., 2009).

Many factors can influence the pyrolysis process, such as the selection of feedstock (particle size, biomass type), reaction conditions (temperature, reaction pressure, heating rate, residence time), and reactor configurations, which can affect the efficiency of heavy metal immobilization in the contaminated soil (Agrafioti et al., 2013). Among these factors, temperature is the key parameter, because higher temperature will cause lower biochar yield (Hossain et al., 2011), cation exchange capacity (Song & Guo, 2012), water sorption capacity (Gaskin et al., 2007) and higher pH, carbon content (Demirbas, 2004), surface area (Han et al., 2016) and more stable heavy metals (He et al., 2010). Devi & Saroha, (2014) pyrolyzed paper mill sludge at the temperature range of 200 - 700℃ , and the heavy metals portioned

into the solid (biochar), liquid (bio-oil) and gas products (biogas) which depended on the pyrolysis temperature and the types of heavy metals. Cetin et al., (2004) studied the physical and chemical structure of chars produced by biomass to explore the effect of heating rate and pressure on pyrolysis. They found that high heating rates and low pyrolysis pressure could help increase char reactivity, change the structure of biomass and influence the physical and chemical structures of char particles. It was also demonstrated that increased pyrolysis pressure contributed to larger char particles and lower total surface area, while higher heating rates might generate larger surface area. The increase of pyrolysis temperature produces biochar with larger surface area, which contributes to higher sorption and enhances soil nutrient and water holding capacity (Tang et al., 2013; Carrier et al., 2012).

2.5 Co-pyrolysis

Although pyrolysis has the potential to reduce the leaching of Cr and transform it to more stable fractions, the pyrolysis process still requires much energy input due to the high temperature demand (300-900 ℃) and the concentration of metals in leachate is still high (Zhang et al., 2009; Huang et al., 2017). Pyrolysis of contaminated soil or sewage sludge can transfer toxic metals to more stable and less toxic fractions (Debela et al., 2012; Jin et al., 2017;). However, concerning the numerous metals and metalloids co-existing in the contaminated site, a more stable and efficient technology should be investigated to reduce the risk of reusing contaminated site (Cheng et al., 2014). Hence, co-pyrolysis of soil enhanced by biomass amendment appears to be a new method to solve soil contamination and utilize energy effectively.

Manara and Zabaniotou, (2012) found some synergistic effects after co-processing of sewage sludge with biomass, including improving the fuel's quality and the processing

efficiency. Furthermore, the mixture of sewage sludge and biomass can result in the dilution of inorganic and toxic compounds. Jin et al. (2017) mixed bamboo sawdust with sewage sludge through a co-pyrolysis process under 400-600 ℃, and observed metals (Cu, Zn, Pb, Cr, Mn and Ni) were transformed to more stable fractions causing the decrease of toxicity and bioavailability of the residual biochar. Moreover, physico-chemical properties were tested before and after experiments, and the results showed that co-pyrolysis would contribute to higher C content and lower biochar yield. Therefore, the co-pyrolysis technology is considered as a practical method for the disposal of heavy metal contaminated sludge, waste or soil to reduce the risk of toxic metals after land application. Debela et al. (2012) found that the leachability of Cd and Zn were reduced after co-pyrolysis of contaminated soil with biomass at 400 ℃. Zhang et al., (2016) pyrolysis chromite-ore-processing residue (COPR) with rice straw to remediate COPR, and the results showed that the volatile fraction, like CO and H_2, played an important role in Cr (VI) reduction during the co-pyrolysis process.

According to the literature, it is recognized that temperature is a more significant factor than duration time (Valo et al., 2004). In addition, it is also accepted that higher temperature contributes to more efficient treatment (Appels et al., 2010). However, economical budgeting in actual site remediation restrains the practicability of high-temperature co-pyrolysis treatment. Tian et al., (2014) investigated the change of organic compounds during pyrolysis of sewage sludge. The sewage sludge was pyrolyzed from 150 to 800 ℃ at different heating rates, and the results showed that most gas was produced at 293−383 °C. In addition, the results also reported that cellulose was more stable than lignin and hemicellulose in biomass and its pyrolysis temperature range was 210–320 ℃. Considering the carbon sequestration efficiency, low temperature pyrolysis (300 ℃) has the potential to produce maximum biochar

yield in the aspect of mass and carbon content (Mohamed et al., 2016). Furthermore, biochar produced at low pyrolysis temperature may contribute to high CEC and surface functional groups (Novak et al., 2009). The existence of aliphatic functional groups during the low temperature pyrolysis process is beneficial to removing inorganic and organic contaminants due to its sorption capacity (Sarmah et al., 2010; Sun et al., 2011).

2.6 Summary

Cr contaminated soil is generated during industrial development, and the remediation of it has been a worldwide concern. Concerning the issue of the contaminated soil, it should be treated or remediated properly due to the risk it may pose to society. It is recognized that removing heavy metals from polluted soils is a difficult mission, so choosing an appropriate remediation technique to limit the harm of Cr is a better alternative (Wuana and Okieimen, 2011). Traditional isolation is a method that only prevents people from contacting with untreated toxicity waste, and it is necessary to monitor the site. Chemical treatment can efficiently remediate polluted sites, but it will contribute to high cost and secondary contaminants. Phytoremediation and bioremediation are methods that can be easily accepted socially by public, but both are time-consuming and need further research to solve existing challenges. In contrast, pyrolysis can efficiently reduce bioavailability of heavy metals and reuse energy generated from biochar during the pyrolysis process. However, using biochars as amendments is still time-consuming and cost-consuming. Therefore, co-pyrolysis seems to be a very promising treatment in terms of effectively and economically reducing toxicity of heavy metals and improving soil quality. According to the literature, only a few researches were done in the remediation of Cr contaminated soil using co-pyrolysis treatment. Hence, Cr

contaminated soil will be co-pyrolyzed with rice straw to immobilize Cr, and then optimal application conditions will be explored in this study.

Chapter 3 Methods and materials

3.1 Soil samples and rice straw preparation

Soil samples used in this study were collected in Shuitou Town, Pingyang, China. This area was highly impacted by tannery wastes, and improperly treated waste and effluents from leather tanning industries have influenced this area for a long time. It was reported that around 9500 tons of Cr-contaminated wastes were produced every year in Shuitou Town (Chen et al., 2012). Soil samples collected in this area were air dried and passed through a 1-mm sieve to remove larger debris. After that, the samples were homogeneously mixed and then stored in sealed plastic bottles at room temperature until use.

Rice straw as a kind of organic material was collected in Tengqiao Town, Wenzhou, China. After collection, the rice straw sample was oven dried, grounded to pass a 1-mm sieve and stored in an airtight container at room temperature.

3.2 Co-pyrolysis reactor

This co-pyrolysis reactor consists of a Parr 4848 Reactor Controller (Parr Instrument Company, Moline, Illinois) and a Series 4530 1L Floor Stand Reactor (Parr Instrument Company, Moline, Illinois) (Figure 3.1). The Reactor Controller brings digital communication to the Floor Stand Reactor. The reactor contains one gas input valve connected to a nitrogen gas cylinder, one gas pressure gauge, a portable 1 L pressure vessel, one gas release valve and one liquid sampling valve. Additional equipment includes a pivoting heating cylinder that is mounted onto the reactor frame and a constant flow of cooling water to protect the heat modules. There are two heating modes programmed in the controller; one of the heating modes is a PID mode controlling the heater output temperature at an adjustable input setpoint and the other mode being a ramp-and-soak mode that is

entered to vary the control of soak times, ramp times and set points. This reactor vessel is capable of pressure to 207 bar (2900 psi) and a maximum operating temperature of 350 ℃ .

Figure 3.1 Principle parts of the co-pyrolysis reactor: Parr 4848 Reactor Controller (left) and Floor Stand Reactor (right)

3.3 Co-pyrolysis procedures

Prior to the co-pyrolysis reaction, initial tests were conducted to gain familiarity with the equipment and materials. Initial tests were useful in developing the best content amounts of the reactor vessel in later testing. Initial testing yielded the best range of temperatures, rice straw / soil mixing ratios, reaction times, pressures and reactor heating modes to develop an appropriate setting ranges and their impacts on the leaching of Cr.

During the main experiments, 30g of prepared soil samples and initially determined ranges of rice straw were thoroughly mixed, prior to placing into the reactor vessel. Two halves of the split ring were put around the head of the vessel, followed by fastening the split ring latches, and lastly, the tightening of the bolts to the split ring. Once the vessel was sealed,

a constant nitrogen flow was used to purge the vessel in the creation of an oxygen free environment. The feedstock mixture was then heated under varied setting conditions, and the heater was removed after the heating cycle is finished to accelerate the cooling of the sample and the vessel. Residual pressure had to be vented into the fume hood before opening the vessel, and an air filter mask should be used due to the chance of foul odours and presence of irritating gas. After the completion of the material processing, the vessel with sample were weighted, the sample removed and stored in an airtight-labeled plastic bag. The soil sample mass remained the same in all the co-pyrolysis treatment runs. Post experimental cleaning of the vessel consisted of filling the reactor vessel with ethyl alcohol followed by a scrubbing with a large test tube brush in preparation for the next treatment.

3.4 Production of co-pyrolyzed char

3.4.1 Char produced at different temperatures

A temperature trial was designed to investigate the effect of co-pyrolysis temperature on the leaching of Cr and the concentration of Cr (VI). The feedstock mixture containing 30 g of soil and 10% of rice straw (mass ratio of rice straw / soil) was used for co-pyrolysis at different temperatures (Table 3.1). To produce co-pyrolyzed char at different temperatures, the controller was set to the assigned temperature, turning on the heating mode. The reaction was retained for 60 minutes once reaching the given temperature. Upon completion of the treatment the heater was removed, and the pressure was released after the vessel cooled down to air temperature. It was theorized that temperature was the key parameter to influence the leaching of Cr and the physical characteristics of produced char. The pressure in the vessel increased with the increasing temperature and the co-pyrolysis process produced as much volatile gas as setting temperature can do. The produced chars after treatments were labelled

and stored in an airtight plastic bag. Each temperature test was conducted in duplicates. It should be noted that the reaction time in this study did not include the heating time.

Table 3.1 Feedstock mixture of soil and rice straw used for co-pyrolyzed char materials in the temperature experiments

Sample ID	Soil mass (g)	Rice straw/soil ratio (%)	Reaction time (min)	Temperature (℃)
Untreated	30	NA	NA	NA
T100	30	10	60	100
T150	30	10	60	150
T200	30	10	60	200
T250	30	10	60	250
T300	30	10	60	300

NA: not applicable.

3.4.2 Char produced at different rice straw/soil ratios

The effect of rice straw addition and its adding amounts were investigated to obtain optimal conditions. Different amounts of rice straw (expressed by rice straw / soil mass mixing ratio) were examined to explore the effects of rice straw addition on reducing the concentration of Cr (VI) and leachable Cr. Therefore, 30 g of soil sample evenly mixed with rice straw at varied ratios (rice straw/soil) was co-pyrolyzed at 200 ℃ and 300 ℃ for 60 minutes, respectively (Table 3.2). The soil sample (30g) without the addition of rice straw indicated the effectiveness of pyrolysis treatment and also revealed the efficiency of co-pyrolysis treatment. The produced chars after treatments were labelled and stored in airtight plastic bags, and each ratio test was conducted in duplicates.

Table 3.2 Feedstock mixture of soil and rice straw used for co-pyrolyzed char materials in the rice straw / soil ratio experiments

Sample ID	Soil mass (g)	Rice straw/soil (%)	Reaction time (min)	Temperature (℃)
R0-200	30	0	60	200
R5-200	30	5	60	200
R10-200	30	10	60	200
R15-200	30	15	60	200
R20-200	30	20	60	200
R0-300	30	0	60	300
R5-300	30	5	60	300
R10-300	30	10	60	300
R15-300	30	15	60	300
R20-300	30	20	60	300

3.4.3 Char produced at different reaction time

In this study, reaction time was defined as the duration time after reaching the assigned temperature. It is theorized that varied reaction time causes the differences in yields and rates among produced solid, liquid and gas. Hence, the reaction time tests sought to investigate impacts on Cr immobilization based on co-pyrolysis treatment using a mix of material (30g of soil and 10% of rice straw) at the temperature of 300 ℃ for various reaction time (Table 3.3). The produced chars after treatments were labelled and stored in airtight plastic bags, and each reaction time test was conducted in duplicates.

Table 3.3 Feedstock mixture of soil and rice straw used for co-pyrolyzed char materials in the reaction time experiments

Sample ID	Soil mass (g)	Rice straw/soil (%)	Reaction time (min)	Temperature (℃)
M10	30	10	10	300
M20	30	10	20	300
M30	30	10	30	300
M40	30	10	40	300
M50	30	10	50	300
M60	30	10	60	300

3.5 Physicochemical characterization of the char by co-pyrolysis of soil and rice straw

3.5.1 Loss-on-ignition (LOI)

During the co-pyrolysis treatment, components of rice straw, including cellulose, hemicellulose and lignin, were transformed to volatile gas. After the vessel cooling down to room temperature, the co-pyrolyzed char and the vessel were weighted to calculate the LOI. The percentage of LOI was calculated as the following formula:

$$\text{LOI}\ (\%) = \frac{A-C}{A-B} \times 100\% \quad (1)$$

where A is the initial weight of feedstock mixture and vessel prior to co-pyrolysis, B is the weight of vessel, and C is the weight of the residual and vessel after co-pyrolysis treatment.

3.5.2 laboratory analyses

3.5.2.1 pH

The pH of char was measured by adding 0.1 M of $CaCl_2$ solution following the procedure of Kalra and Maynard (1991). 10 g of each sample was placed in a beaker by adding 20 ml of 0.1 M of $CaCl_2$ solution, and then a glass rod was used to stir every 5 minutes for 30 minutes. Settling for 30 minutes, the electrode of pH meter was immersed into the supernatant solution. It was noted that the pH meter should be calibrated with two buffers (pH 4.0 and 7.0 buffers) and should be checked and recalibrated against buffers before measurement and after 5 samples.

3.5.2.2 Cation exchange capacity (CEC) measurement

According to the pH of soil sample, the sodium acetate solution was chosen as an extracting reagent. The 0.5g of sample was weighted and transferred to a 50-mL, tightly-stoppered centrifuge tube. Each tube was added with 20 mL of 1.0 N NaOAc solution, and then shaken in a mechanical shaker for 5 minutes. The solid and liquid were separated by centrifuge until the supernatant liquid was clear, and the liquid was discarded. This procedure was repeated three more times. Afterwards, 20 mL of 1.0 N NH_4OAc solution was added, repeating the shake and centrifuge procedure as before. The supernatant was continuously decanted into a 100 mL volumetric flask until reaching the 100 mL mark, and then determined the concentration of Na^+ using emission spectroscopy.

3.5.2.3 Organic matter

Organic matter was estimated by weight loss. The porcelain crucibles were heated at 375 ℃ for an hour to remove water and weighted before use. The sample (1 g) was placed in that pre-weighted crucible, heated in a muffle furnace at 600 ℃ for three hours, then waited

to cool down and weighted. The heating procedure was repeated until the weight without change.

3.5.2.4 pH of Point of Zero Charge (pH_{PZC}).

The initial pH was adjusted using a pH meter to 2, 4, 6, 8, 10 with 0.1 M HNO_3 and 0.1 M NaOH. A 20 mL of different initial pH and 0.5 g of weighted sample was added to a 250 mL Erlenmeyer flask. All the Erlenmeyer flasks were shaken in a revolving water bath (25 ℃) for 24 h to reach equilibrium. Afterwards, the result pH was measured, and the point of intersection between the initial pH and result pH was the value of pH_{PZC}.

3.5.2.5 The total concentration of Cr

The total concentration of the soil sample and the samples after co-pyrolysis were conducted using microwave digestion. This microwave digestion method was faster, safer, and controlling heating conditions better than conventional digestion methods. Each weighted sample (0.1 g) was transferred into the microwave vessel, and 6 mL of HNO_3, 2 mL of HF and 2 ml of H_2O_2 were added, respectively. Then, the samples were sufficiently digested in the microwave oven (Anton Paar Inc, USA) at 180 ℃ lasting for 1 h. This procedure was repeated until samples were completely digested, and the concentration of Cr was determined by flame atomic absorption spectrometer (FAAS) (AA800, PerkinElmer, USA).

3.5.3 Leaching test

Taking into consideration that co-pyrolysis treatment was not able to reduce or extract the Cr from contaminated soil, the mobile amount of Cr could be measured to indicate the effectiveness of the remediation. Therefore, a batch synthetic precipitation leaching procedure (SPLP) (US EPA, 1994) was conducted on the samples to assess the efficiency of

the co-pyrolysis treatment on Cr immobilization in the contaminated soil. SPLP with minor modification was followed in this test (US EPA 1994). The pyrolyzed samples (2 g of each) were filled into glass jars and mixed with 40 mL leaching solution (a 60/40 mix of H_2SO_4 and HNO_3 diluted with double deionized water to pH of 4.2 ± 0.05). The samples were then shaken for 18 h using a horizontal shaker and filtered through a 0.45 μm membrane filter. The filtrate was acidified with HNO_3 to pH < 2.0 and the concentration of Cr in the leachate was determined by flame atomic absorption spectrometer (AA800, PerkinElmer, USA).

3.5.4 The concentration of total Cr(VI)

It was essential to determine the content of Cr(VI) before and after co-pyrolysis treatment, since the reduction of Cr(VI) could more directly assess the efficiency of the co-pyrolysis treatment on Cr immobilization. Although measuring the amount of Cr(VI) in aqueous solution was an easy way, the total concentration of Cr(VI) in solid could be more accurate and direct indicating decreased toxicity of Cr. Therefore, the concentration of total Cr(VI) was conducted according to the method US EPA 3060A. A 2.5 g of pyrolyzed char was digested using 50mL alkaline extracting solution (a mix of 20 g of NaOH and 30 g of $NaCO_3$ diluted with double deionized water to 1 L in a volumetric flask) in a 250mL Erlenmeyer flask, and mixed with approximately 400 mg of $MgCl_2$ and 0.5 mL of 1.0 M phosphate buffer. The mixture was heated at 90-95 ℃ for 90 min with continuous stirring, and then transferred to the filtration apparatus that a 0.45 μm membrane filter was used for filtration after cooling down to room temperature. The filtrate was adjusted to pH 7.5 with the addition of 5.0 M HNO_3 and diluted to 100 mL with double deionized water. Any flocculent precipitate formed should be filtered before dilution. The total Cr(VI) in dissolved filtrate was determined colorimetrically by reaction with diphenylcarbazide (US EPA 7196A).

2 mL of diphenylcarbazide solution was mixed with the filtrate and the pH was adjusted to 2 ± 0.5. The mixture was then diluted to 100 ml and placed 10 min for full color development. An appropriate portion of the solution was transferred to a 1-cm absorption cell and measured at 540 nm for its absorbance. Both soluble and insoluble matrix spikes were used as quality control to ensure the accuracy of the extraction procedure.

3.5.5 BCR sequential extraction experiments

The bioavailability and toxicity of Cr could be indicated by its chemical speciation (Huang and Yuan, 2016), and this could be determined by BCR sequential extraction scheme (Chen et al., 2008). Although BCR sequential extraction experiment was a chemical method which may not provide accurate Cr speciation in the soil, it was still useful for monitoring the relative Cr species change, as a consequence of co-pyrolysis treatment. Therefore, the Cr in the samples before and after co-pyrolysis treatment was sequentially extracted referring to the modified three-step BCR method proposed by Rauret et al. (1999). Through BCR sequential extraction, the fractions of Cr were divided into four categories: exchangeable and acid-soluble (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions. F1 and F2 were more mobile fractions because they were very prone to be uptake by plants or leaching in water. F3 was identified as potential toxic species due to its rigorous requirements for degradation and F4 was usually recognized as non-bioavailable and relatively stable species (Devi and Saroha, 2014; Fuentes et al., 2008). Due to the high concentration of Cr in the soil, small dry mass of samples (0.2 g of each sample) were extracted in centrifuge tubes with the corresponding extracting solutions. The detailed extraction procedures were described below.

In step 1, 0.2 g of sample was transferred to centrifuge tube and mixed with 40 mL of acetic acid (0.11 mol l^{-1}), shaken overnight. The tube was then centrifuged, and the extract

was isolated and stored in a refrigerator at 4 °C for analysis. In step 2, 40 mL of hydroxylamine hydrochloride (0.5 mol l^{-1}) was added to the residue of step 1, and then the suspension liquid was extracted as described in step 1. In step 3, 10 mL of hydrogen peroxide was carefully added to the residue of step 2 and digested at room temperature for 1 h with occasional manual shaking, before digesting at 85 ± 2 ℃ in a water bath. When hydrogen peroxide was evaporated to less than 3 mL, this procedure was repeated with further addition of 10 mL hydrogen peroxide. The samples were then heated to nearly dry and cooled down to room temperature. The extraction was continued with the addition of 50 mL of ammonium acetate (1.0 mol l^{-1}) and separated the extract as in step 1. In step 4, the residue from step 3 was transferred to microwave vessels and digested, and the Cr concentration was determined following the same procedure described in Section 3.5.2.5.

3.5.6 Time-varying desorption kinetics

To further investigate the Cr release by different extractants, time-varying desorption experiments were conducted. Three different kinds of extractants (organic acid, inorganic acid, contrastive extractant) were used in this test, and these extractants had different impacts on Cr release. Extractants included organic acid (10 mmol L^{-1} citric acid), inorganic acid (10 mmol L^{-1} nitric acid), and contrastive extractant (10 mmol L^{-1} $CaCl_2$). Citric acid, which is commonly present in the rhizosphere soil due to the decomposition of plants and animal residue, has the ability to accelerate the dissolution and bioavailability of heavy metals (Han et al., 2004; Lim et al., 2004). Nitric acid is from the decomposition of microbial metabolites, and $CaCl_2$ was chosen as a contrastive extractant because it is similar with soil solutions. 1 g of sample was mixed with 20 ml corresponding extractant, and equilibrated at 25 ℃ for 0.5, 1, 4, 15, 27, 45, 60, and 76 h. All the samples were centrifuged and collected for analysis by

FAAS. The desorption Cr in the samples was described as pseudo-first-order (Eq. 2) or pseudo-second-order (Eq. 3) kinetic equations:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where: q_e was the equilibrium amount of released Cr; q_t was the concentration of Cr released at time t; k_1 and k_2 are the rate constant of pseudo-first-order and pseudo-second-order, respectively.

3.5.7 Bioaccessibility of Cr

In this study, bioaccessibility was referred to the concentration of Cr that would potentially be adsorbed by gastrointestinal system. Although BCR sequential extraction was determined to explore the Cr species and potential bioavailable Cr, it still did not provide a direct and good indication of human bioaccessibility. For many decades, numerous researches were performed to explore the fraction of potential toxic elements in soil which could be uptake by plants or crops (Kisku et al., 2000). However, metals in the urban soil could be easily transferred to human especially children through ingestion, breathing or skin contact. Ljung et al. (2006) found that it was a common behavior for children aged 18 months to 2 years ingesting soil through hand-to-mouth activity. Therefore, scientists tried to develop simple extraction tests involved in simulating gastrointestinal tract fluids at physiological pH and temperature (Wragg and Cave, 2003). Although many in vitro chemical extraction methods were developed to assess the metal bioaccessibility, such as HCl extractions, Relative Bioaccessibility Leaching Procedure (RBALP), Simple Bioaccessibility

Extraction Test (SBET) and Physiologically Based Extraction Test (PBET) (Izquierdo et al., 2015), the SBET and PBET were methods commonly used in the literatures (Meunier et al., 2011; Luo et al., 2012). It was reported that the content of bioavailable metal in the gastric phase determined by the SBET method was in agreement with that in the same phase measured by PBET (Oomen et al., 2002; Poggio et al., 2009). Although these methods simulating gastrointestinal conditions could not be recognized as accurate conditions in the gastrointestinal system, the data obtained could also present valuable data for risk assessments.

In this study, the bioaccessibilities of Cr in the samples were determined following the SBET method, which was an in vitro leaching procedure designed to assess the amount of absorbed metals in the stomach digestive system in humans (Ruby et al., 1999). The extracting solution was glycine (0.4 mol L^{-1}) adjusted to pH 1.5 with HNO_3, which was used to simulate the most aggressive human gastric system. 0.2 g of sample with the addition of 20 mL prepared glycine solution was placed in a rotating horizontal shaker at 37 ± 2 ℃ to simulate stomach mixing. After 1 h, each mixture was centrifuged, and supernatant was collected for analysis by FAAS.

3.5.8 Characterization of char samples

The specific surface area, pore volume and pore diameter of samples under different heating conditions were determined by the Brunauer–Emmett–Teller (BET) method using a BELSORP-max (BEL Japan, Inc.). 0.2 g of dried sample was heated for 3 h at 573K under evacuation before measurement and was analyzed through nitrogen adsorption isotherms at 77K. Fourier-transform infrared (FTIR) analysis of the samples was measured by a Bruker Tensor 27 FTIR spectrophotometer (Bruker Corporation, Billerica, USA). The dried sample

(1 mg) was pressed with 100 mg dried potassium bromide (KBr), and signal beam was recorded within 4000-400 cm^{-1} wavelength range to determine functional groups. The surface morphology and mineral component of chars before and after co-pyrolysis were studied by scanning electron microscopy (SEM) using a XFlash 6T | 30 (Bruker Corporation, Billerica, USA) and X-ray diffraction (XRD) using a Bruker D8 Advance (Bruker Corporation, Billerica, USA).

3.5.9 Statistical analyses

Statistical analysis was performed with the software SPSS. Analysis of variance (one-way ANOVA) was conducted to compare the changes of different co-pyrolysis treatments. Where significant p-value were lower than 0.05, differences between individual means were tested using the least significant difference (LSD) test.

Chapter 4 Results and discussion

4.1 Initial test results

Initial tests were conducted to explore the impacts of different conditions (temperatures, rice straw / soil ratios, reaction time, pressures and reactor heating modes) on the leaching of Cr, and the results were shown in Table 4.1. Compared to I5 (ramp-and-soak mode), I3 conducted in PID mode was more effective in reducing Cr leaching. Also considering the less time and energy cost, PID mode was selected in the following study. All pyrolysis treatments, with or without rice straw addition, showed no significant changes ($P > 0.05$) in Cr leaching with increasing initial pressures. For example, there was no significant change of Cr in leachates between I3 and I1 treatment, and no significant difference between I10 and I13 treatments. However, at different pyrolysis temperatures, rice straw addition and reaction time were found to be influential to the leaching of Cr. For instance, the concentration of Cr leaching in I12 and I8 reduced from 25.47 mg kg^{-1} to 7.71 mg kg^{-1} with the temperature increase from 200 ℃ to 300 ℃ . Compared to I3, the Cr leaching in I8 declined about 50 % with the addition of 20 % rice straw, from 14.45 mg kg^{-1} to 7.71 mg kg^{-1}. Moreover, with the pyrolysis reaction time increase, the concentration of Cr in leachates increased from 11.29 mg kg^{-1} to 14.45 mg kg^{-1}, which was the opposite trend from what was expected. Therefore, the parameters of temperature, rice straw addition ratio and reaction time were chosen to explore the impacts to the leaching and speciation of Cr.

Table 4.1 Initial test results for exploring optimal conditions

Sample ID	Description	Temperature (℃)	Initial pressure (MPa)	Reaction time (min)	Leached Cr[#] (mg kg^{-1})
I1	30 g soil	300	1.5	60	14.52±0.39
I2			1	60	13.91±0.74
I3			0.5	60	14.45±1.50
I4			0.5	40	11.29±2.21
I5	30 g soil (ramp-and-soak mode*)	300	0.5	60	15.67±0.63
I6	30 g soil, 20% rice straw	300	1.5	60	7.56±0.28
I7			1		6.48±0.56
I8			0.5		7.71±1.97
I9			0.11		7.04±0.08
I10	30 g soil, 20% rice straw	200	1.5	60	26.89±0.80
I11			1		26.56±1.27
I12			0.5		25.47±2.54
I13			0.11		27.01±2.49

* Ramp-and-soak mode could set soak times, ramp time and setting points, and it was used for sample I3 only. All the other samples were tested in PID mode, which could reach setting temperature as soon as possible.

[#] SPLP test was conducted to determine the concentration of leachate Cr.

4.2 Results of loss-on-ignition (LOI)

The LOI value of the samples under different pyrolysis temperature was shown in Table 4.2. It was obvious that the mass loss of ignition increased ($P < 0.05$) with elevated pyrolysis temperature due to the volatilization of organic matter, and LOI increased rapidly around 200 ℃. Theoretically, pyrolysis of rice straw could be divided into three phases, i.e., moisture evaporation (temperature < 200 ℃), main devolatilization (temperature 200–350 °C), and continuous devolatilization (temperature > 350 °C) (Zhang et al., 2009). Results indicated that the loss of mass at temperatures of 100-150 °C may be due to water transforming to a gaseous phase, and rapid increase of LOI above 200 °C may have resulted largely from decomposition of hemicellulose and cellulose (Zhang et al., 2009). Ahmad et al (2014) also found ash content increased with the increasing temperature and indicated that was mainly due to the removal of organics in the alkaline minerals and organic matter. The LOI of chars produced at different feedstock ratios were summarized in Table 4.3, and a similar trend as LOI of chars produced at different temperatures was found. As the addition ratio of rice straw rose from 0 % to 20 %, the mass loss of the char increased after pyrolysis treatments (Table 4.3), while longer reaction time did not significantly influence the LOI value ($P>0.05$) (Table 4.4). This was in accordance with the previous explanation that rice straw would transfer to gas during pyrolysis treatments and the elevated addition of rice straw would increase the percentage of volatile organic matter.

Table 4.2 LOI of different temperature produced char

Sample ID	Descriptions	Reaction time (min)	Co-pyrolysis temperature (℃)	LOI (%)
Untreated	30g soil, 3g* rice straw	60	NA	NA
T100	30g soil, 3g* rice straw	60	100	3.64±0.43
T150	30g soil, 3g* rice straw	60	150	3.94±0.56
T200	30g soil, 3g* rice straw	60	200	6.67±0.82
T250	30g soil, 3g* rice straw	60	250	8.79±1.29
T300	30g soil, 3g* rice straw	60	300	10.0±0.95

*Addition of rice straw was based on the mass of soil, i.e., 3 g rice straw was 10 % of 30 g soil.

Table 4.3 LOI of different ratio of rice straw produced char

Sample ID	Descriptions	Reaction time (min)	Co-pyrolysis temperature (℃)	LOI (%)
R0-200	30g soil, 0% rice straw	60	200	3.67±0.31
R5-200	30g soil, 5% rice straw	60	200	6.19±0.00
R10-200	30g soil, 10% rice straw	60	200	6.67±0.12
R15-200	30g soil, 15% rice straw	60	200	8.86±0.97
R20-200	30g soil, 20% rice straw	60	200	8.06±0.64
R0-300	30g soil, 0% rice straw	60	300	5.33±0.09
R5-300	30g soil, 5% rice straw	60	300	7.30±0.49
R10-300	30g soil, 10% rice straw	60	300	10.0±0.95
R15-300	30g soil, 15% rice straw	60	300	11.30±0.07
R20-300	30g soil, 20% rice straw	60	300	12.22±0.33

Table 4.4 LOI of different reaction time produced char

Sample ID	Descriptions	Reaction time (min)	Co-pyrolysis temperature (℃)	LOI (%)
M10	30g soil, 3g* rice straw	10	300	8.79±0.44
M20	30g soil, 3g* rice straw	20	300	8.48±0.26
M30	30g soil, 3g* rice straw	30	300	9.39±0.01
M40	30g soil, 3g* rice straw	40	300	8.79±0.52
M50	30g soil, 3g* rice straw	50	300	9.09±0.01
M60	30g soil, 3g* rice straw	60	300	10.0±0.95
M90	30g soil, 3g* rice straw	90	300	9.85±0.00

*Addition of rice straw was based on the mass of soil, i.e., 3 g rice straw was 10 % of 30 g soil.

4.3 Properties of selected samples

The properties of soil sample and representative co-pyrolyzed chars in this study were shown in Table 4.5. The total Cr of the untreated soil sample was 36433.20 mg kg^{-1}, which indicated this soil was highly contaminated by Cr. A little increase was found in soil pyrolyzed at 300 ℃ without rice straw addition due to the loss of water and organic matter. However, the amount of total Cr slightly decreased while the Cr-contaminated soil was pyrolyzed with rice straw at 300℃. This soil was slightly alkaline at pH 7.95 and an increase in pH of the soil ($P < 0.05$) was found after pyrolysis at 300 ℃ for 60 min. With the addition of rice straw to the soil sample, the pH value was increased from 8.31 to 8.49 ($P < 0.05$). This increasing trend in pH could be explained that alkali salts were separated from the organic matrix after pyrolysis treatment (Maiti et al., 2006). A higher pH value is more likely to restrain heavy metal release. Another possible reason may be that amine functionalities

transformed into pyridine-like compounds and acidic surface functional groups decreased with the increasing temperature (Chen et al., 2014). Moreover, a highly positive correlation between pH value and pyrolysis temperature was reported (Jin et al., 2016). The CEC is usually used to describe the potential of samples to reversibly adsorb positively charged species (Brewer et al., 2011). In this study, the CEC of untreated soil sample was 189.739 cmol/kg and that of co-pyrolyzed chars rose ($P < 0.05$) to 199.032 cmol/kg in R0-300 and 201.901 cmol/kg in R10-300. However, the differences of CEC between R0-300 and R10-300 were not significant ($P > 0.05$). Similar results were found by Houben et al., (2013) who observed a slight increase in CEC with the increase of added biochar. In addition, the increase value of CEC with the increased pyrolysis temperature may be caused by the elevated concentration of cationic elements, which were not volatile during the process (Al-Wabel et al., 2013; Bandara et al., 2017). Higher CEC is helpful to adsorb and retain cations (e.g. Mg^{2+}, k^{+}, Ca^{2+}) and enhance the nutrient holding capacity of the soil. As expected, the content of organic matter was notably decreased ($P < 0.05$) from 17.87% to 10.76% after pyrolysis treatment, and this phenomenon was due to the decomposition and conversion of organic matter at high pyrolysis temperature. It was also noteworthy that organic matter in sample R10-300 was a little more than that in R0-300, which was likely led by the addition of rice straw. Compared to untreated soil, the specific surface area and total pore volume in R0-300 and R10-300 reduced, while the mean pore diameter increased. Similar results were observed by Huang et al. (2017) who found the addition of rice straw during the pyrolysis of sewage sludge slightly decreased the surface area, pore size and pore volume of pyrolyzed chars. The reason of this phenomenon could be the production of ash and oil. Song and Guo (2012) also found low BET surface areas in poultry litter biochar because of ash filling or blocking pores of biochar. In addition, Cetin et al. (2005) found the effects of pressure to the

pore structure of produced char. Therefore, the pressure (0.5 MPa) applied in this study may be one of the reasons for increased pore diameter. Moreover, higher temperature could widen micropore to mesopore or macropore due to the dehydration and aromatization of the carbon skeleton, which would reduce surface area (Zhao et al., 2017). The value of pH_{PZC} in raw soil sample was 9.40, and it increased a little after pyrolysis at 300℃. Besides, the value of pH_{PZC} also grew in R10-300 with the addition of rice straw, and the pH_{PZC} of each sample was substantially above the initial pH. Uchimiya et al. (2011) reported that increasing pyrolysis temperature contributed to higher values of pH_{PZC}, which was in accordance with the results in this study.

Table 4.5 Properties (mean ± standard deviation) of the soil sample and representative samples

Sample ID	Total Cr (mg kg^{-1})	pH	CEC (cmol kg^{-1})	Organic matter (%)	pH_{PZC}	BET (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Mean pore diameter (nm)
Untreated	36433.20±6728.79	7.95±0.01 [a]	189.74±0.96 [a]	17.87±0.00 [a]	9.40	39.02	0.093	9.53
R0-300*	37957.18±6902.63	8.31±0.03 [b]	199.03±2.23 [b]	10.76±0.01 [b]	9.42	22.53	0.076	13.53
R10-300#	36298.80±7294.19	8.49±0.01 [c]	201.90±6.66 [b]	12.25±0.01 [b]	9.65	18.01	0.076	16.82

* 30 g of soil sample was pyrolyzed at 300℃ for 60 min without the addition of rice straw.

30 g of soil sample was co-pyrolyzed with 3g rice straw at 300℃ for 60 min.

In each column, means followed by same letter were not significant ($p>0.05$).

4.4 Results of SPLP

Co-pyrolysis temperature is a key parameter affecting the behavior of rice straw and thus subsequently influences the leaching of Cr after co-pyrolysis treatments. The results of the SPLP test for Cr in the soil samples after co-pyrolysis with 10 % of rice straw under different temperatures were shown in the Figure 4.1. It was noteworthy that the Cr leaching amounts in the untreated soil sample was very high (166.30 mg kg^{-1}), which could be ascribed to the fact that the soil sample collected was highly impacted by tannery wastes. As expected, the leaching of Cr in the co-pyrolyzed residues was found to be at least three times lower compared with that in the untreated soil sample and significantly decreased ($P < 0.05$) with elevated co-pyrolysis temperature. Besides, the leachable Cr was decreased (about 81 %) by increasing temperature from 100 ℃ to 300 ℃. When the pyrolysis temperature increased from 100 ℃ to 150 ℃, a significant decline ($p<0.05$) in Cr leaching was observed in the soil sample with 10 % rice straw addition. Figure 4.2 presented the concentration of leachable Cr in soil co-pyrolyzed with different ratios of rice straw. Overall, the leaching of Cr in pyrolyzed chars, with or without rice straw, was lower (decreased up to 95 %) than untreated soil sample (166.30 mg kg^{-1}). Considering pyrolysis of soil sample without rice straw addition, the leachable Cr decreased from 19.51 mg kg^{-1} to 14.45 mg kg^{-1} with the temperature increase from 200 ℃ to 300 ℃. All co-pyrolysis treatments at 200 ℃ with different amounts of rice straw addition were found to have an obvious fluctuation in Cr leaching. This phenomenon may be due to incomplete devolatilization of rice straw at 200 ℃, causing various impacts in Cr leaching. By contrast, increasing the addition of rice straw in co-pyrolysis treatment at 300 ℃ could significantly decrease ($P < 0.05$) the level of Cr (up to 47%) in leachates.

According to initial test results (Table 4.1), the Cr leaching level in I4 (11.29 mg kg^{-1}) was less than that in I3 (14.45 mg kg^{-1}). Hence, reaction time experiments were conducted to explore an appropriate reaction time for reducing the leaching of Cr, and the results were shown in Figure 4.3. The extension of the reaction time during the co-pyrolysis of soil and 10% rice straw did not give obvious alleviation of the Cr leaching. In other words, there was a slight increase of the Cr leaching when reaction time was within 40 min, but the leaching of Cr in 60 min was similar with that in 10 min. This may be due to the complete devolatilization of added rice straw before the temperature reaching at 300 ℃, and afterwards longer reaction time did not have significant effects on Cr leaching.

According to the Identification Standards for Hazardous Wastes-Identification for Extraction Toxicity in China (GB5085.3-2007), the leaching of Cr in this study was far below the allowable Cr leaching concentration (15 mg L^{-1}). For example, 166.30 mg kg^{-1} of leachable Cr in untreated soil is equivalent to 8.25 mg L^{-1} of Cr in the corresponding leachate. It was also reported by Zhou et al. (2018) that the total concentration of Cr was high but lower in the leachate. The decrease of leachable Cr after co-pyrolysis treatments could be ascribed to the degradation of organic matter and the formation of undissolved compounds with calcium, copper and alkali. Overall, the soluble Cr was transferred to more stable and insoluble forms after co-pyrolysis treatments (Gao et al., 2017). The results of SPLP leaching tests indicated that temperature played an important role in reducing the leaching of Cr and the rice straw addition at a higher co-pyrolysis temperature (300 ℃) could significantly reduce the leachable Cr that harms the environment.

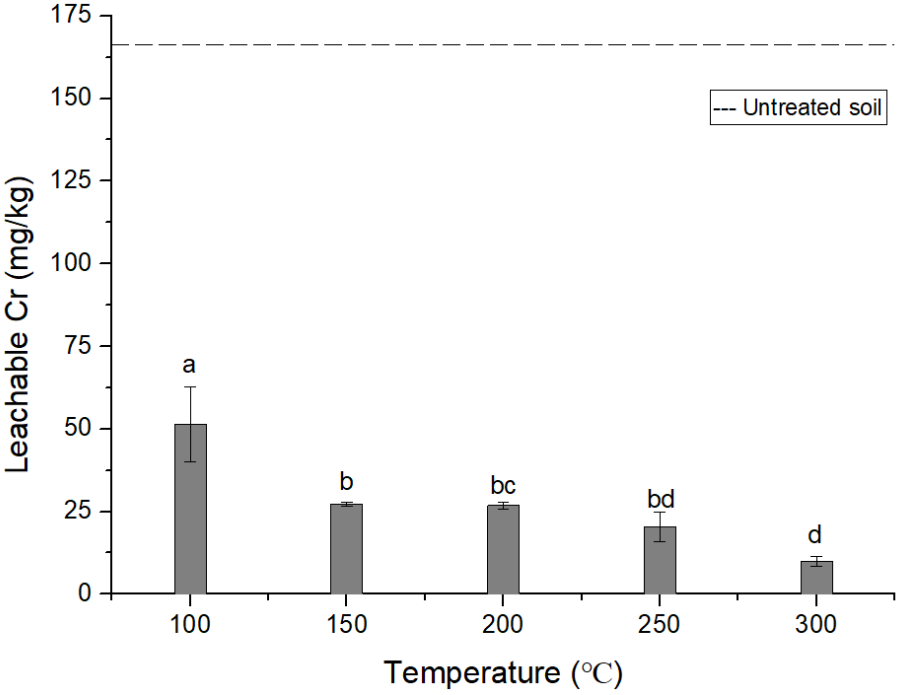


Figure 4.1 SPLP of Cr in the soil after co-pyrolysis with 10% of rice straw under different temperatures (n=4, $p < 0.05$). Means followed by similar letter were not significant different (P>0.05).

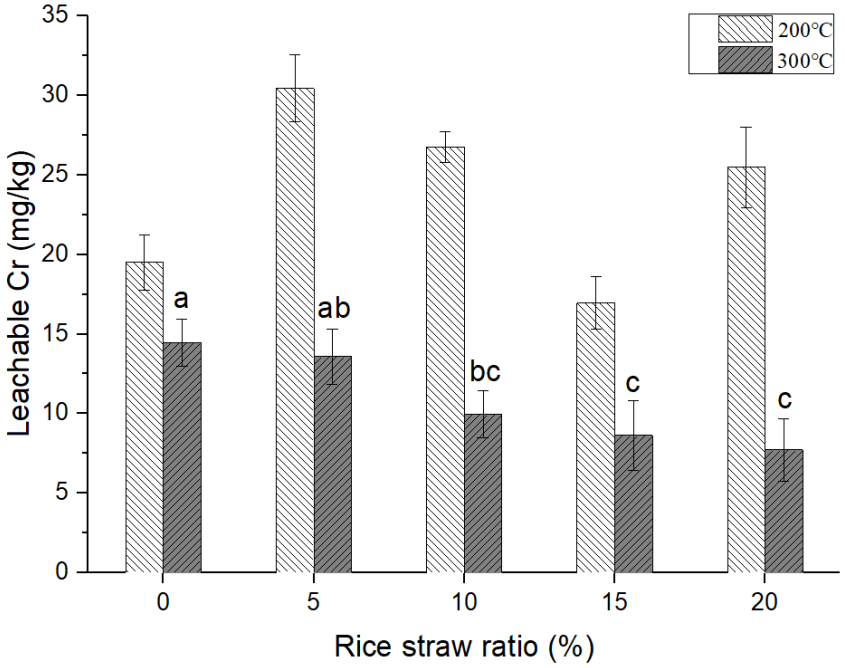


Figure 4.2 SPLP of Cr in the soil after co-pyrolysis under 200 ℃ and 300 ℃ at various ratios of rice straw (n=4). Means followed by similar letter or no letter were not significant different (P>0.05).

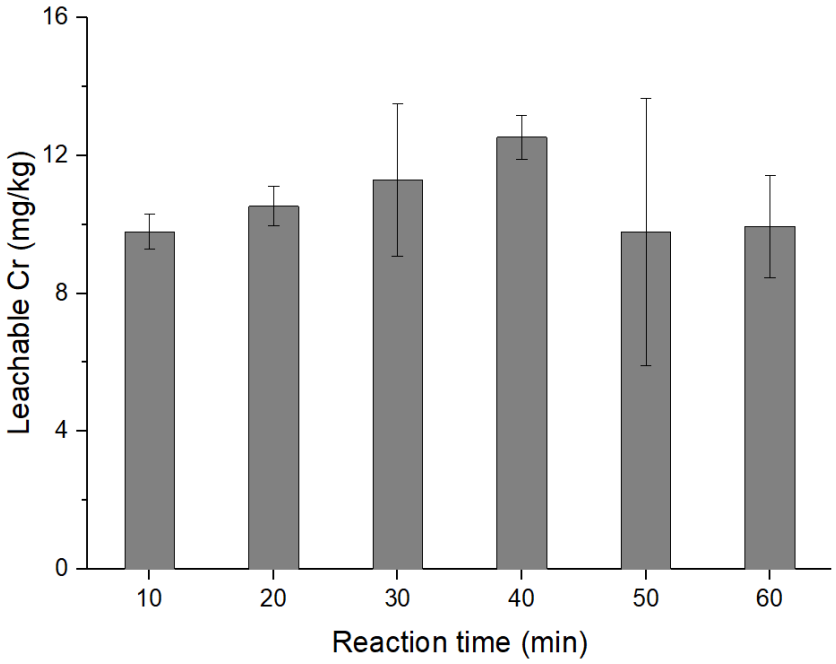


Figure 4.3 SPLP of Cr in the soil after co-pyrolysis with 10% rice straw under 300 degree at various reaction time (n=4, p>0.05)

4.5 Total contents of Cr(VI)

Figure 4.4 showed the total contents of Cr(VI) in the mixture of Cr contaminated soil and rice straw co-pyrolyzed at different temperatures. The content of Cr(VI) in the untreated soil was 407.5 mg kg^{-1}, which was not surprising due to the high concentration of total Cr in this soil sample. Compared to Canadian Soil Quality Guidelines (CCME, 1999), the content of Cr(VI) in this study was about 1018 times higher than the criteria (0.4 mg kg^{-1}) of Cr(VI) in soil used for agriculture. It can be seen from the figure that the Cr(VI) content significantly decreased (73%) ($P<0.05$) from 267.8 mg kg^{-1} to 73.0 mg kg^{-1} when temperature increased from 100 ℃ to 300 ℃ . This trend was in agreement with the results observed by Zhang et al. (2009) who found high pyrolysis temperature had beneficial effects in Cr(VI) reduction, and explained it in triplicate ways: (1) volatilization of more organic compounds; (2) more reaction between the Cr(VI) and organic compounds; (3) gaseous organic matter diffusion in

the sample. Comparing temperature of 100 ℃ to 150 ℃, the reduction of Cr(VI) was not significant. The former phenomenon may correspond to the previous results that LOI decreased slowly at temperatures below 150 ℃ due to moisture evaporation, which resulted in an insignificant reduction of Cr(VI).

The total content of Cr(VI) with the different addition ratio of rice straw were shown in Figure 4.5. Without the addition of rice straw, the total concentration of Cr (VI) was lower than that in untreated soil (407.5 mg kg^{-1}), which indicated that only pyrolysis of soil without the additive could efficiently reduce Cr (VI). On the whole, all pyrolysis treatments at 300 ℃, with or without rice straw addition, resulted in less content of Cr(VI) as compared to all pyrolysis treatments at 200 ℃. Furthermore, the effect of rice straw addition in Cr(VI) reduction (52%) at 200 ℃ was more obvious than that at 300 ℃ (33%). The results were in agreement with Zhang et al. (2016) who found the increase of cellulose contributed to the elevated Cr(VI) reduction percentage (CRP). They also reported that the addition of rice straw could increase the amount of volatile organic fraction, which was helpful to reduce Cr(VI), until a high rice straw ratio was obtained. A further increase in the ratio had little impacts on Cr(VI) reduction.

As shown in Figure 4.6, the reduction of Cr(VI) fluctuated with increasing pyrolysis reaction time, and the reaction time did not show significant effects on the Cr(VI) reduction. This was not in agreement with the results observed by Zhang et al. (2016) who found the CRP increased with longer reaction time, and it increased sharply from 1 min to 5 min. The reason could be the competition of Cr(VI) reduction during the temperature-rise period.

Overall, pyrolyzed soil without the addition of rice straw decreased Cr(VI) by 34 % and 79 % in R0-200 and R0-300, respectively. With the synergistic effect of rice straw addition, the Cr(VI) content decreased by up to 86% in R20-300 compared to untreated soil.

Both increased pyrolysis temperature and rice straw addition could effectively transform Cr(VI) to Cr(III). As already mentioned, the pH value increased after co-pyrolysis treatment, which may be caused by the release of acidic surface groups such as -COOH and -OH and carbonates formation ($CaCO_3$ and $MgCO_3$) during pyrolysis (Méndez et al., 2013; Yuan et al., 2014). Wang et al. (2015) reported that electrostatic interaction between Cr(VI) ions and acidic oxygen-containing functional groups could facilitate Cr(VI) adsorption and help reach equilibrium in a short period. Additionally, volatilized organic matter reacting with Cr(VI) could also effectively reduce Cr(VI) amounts (Zhang et al., 2009).

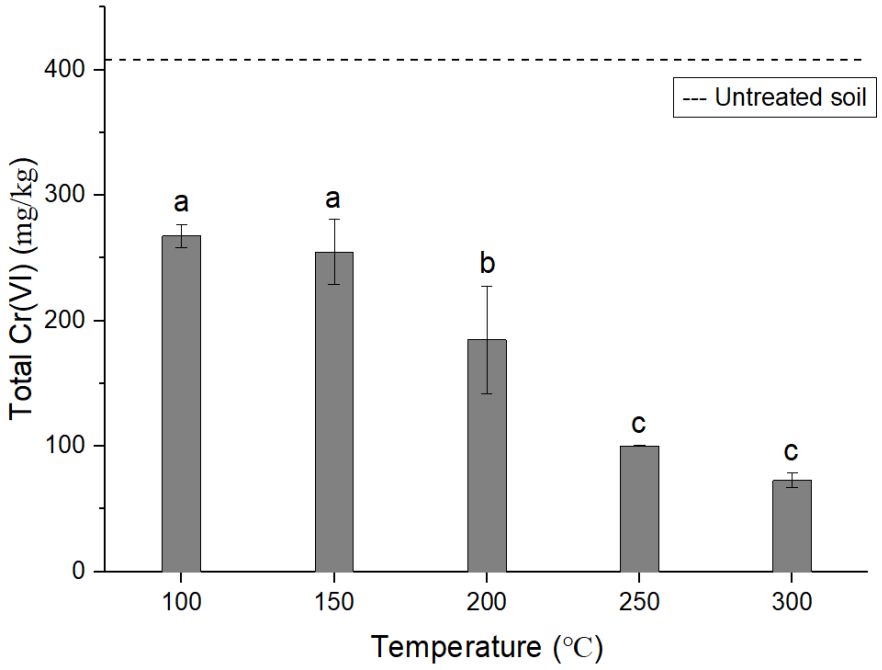


Figure 4.4 The concentration of Cr(VI) in the soil after co-pyrolysis with 10% of rice straw under different temperature (n=2, $p<0.05$). Means followed by similar letter were not significant different ($P>0.05$).

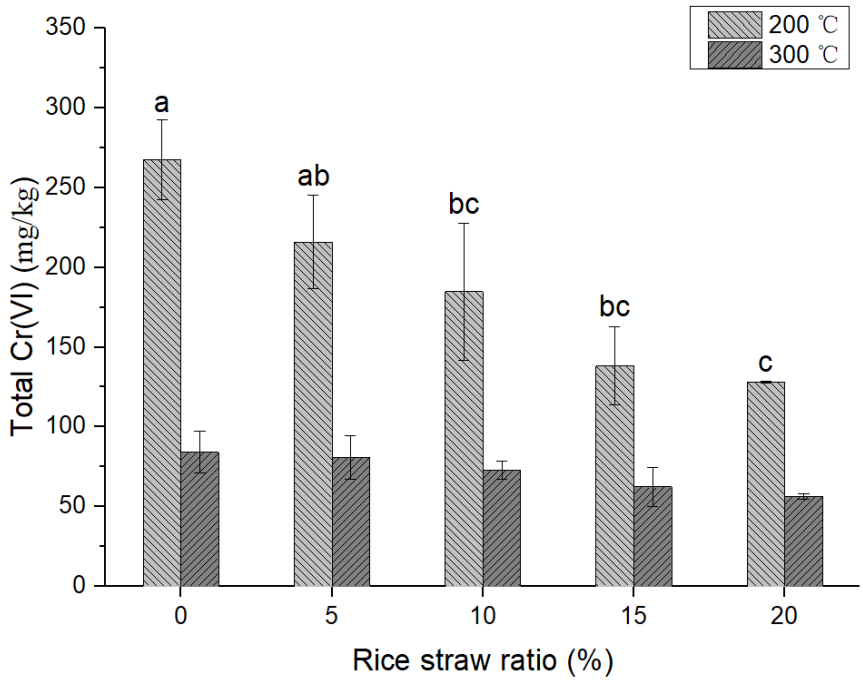


Figure 4.5 The concentration of Cr(VI) in the soil after co-pyrolysis under 300 ℃ and 200 ℃ at various ratios of rice straw (n=2). Means followed by similar letter or no letter were not significant different (P>0.05).

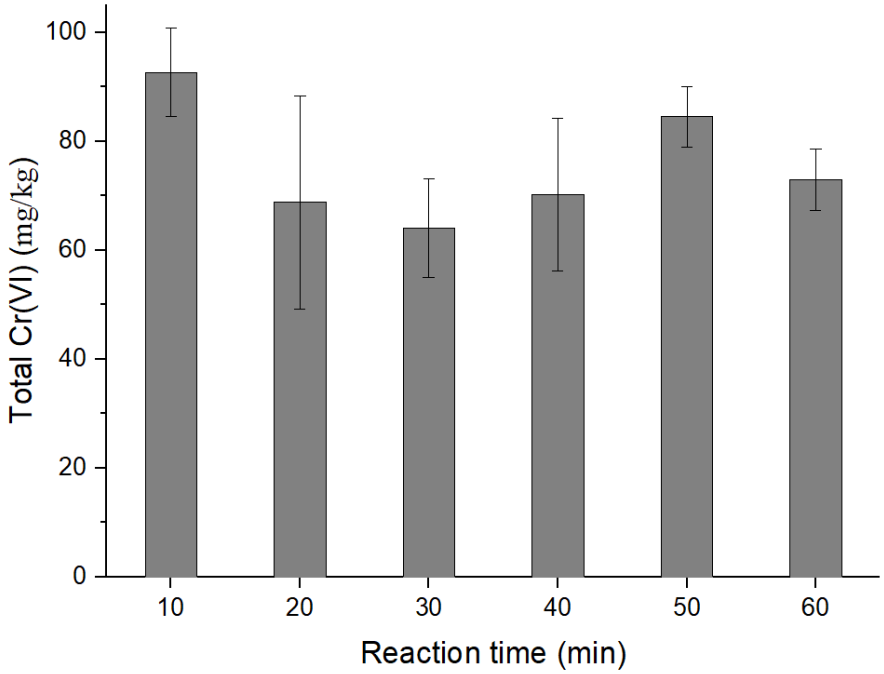


Figure 4.6 The concentration of Cr(VI) in the soil after co-pyrolysis with 10% rice straw under 300 ℃ at various reaction time (n=2, p>0.05)

4.6 BCR results

The distribution of Cr in the four BCR fractions in the untreated soil and co-pyrolyzed samples were shown in Figure 4.7(a, b and c). It was reported that the mobilization of Cr fraction decreased in the following order: F1 > F2 > F3 > F4 (Huang and Yuan, 2016). As shown in the figures, it could be easily noticed that the most Cr was in the form of the F4 fraction, which accounted for more than 80 % of total concentration of Cr in all the untreated and treated samples. Meanwhile, the F2 fraction was relatively high compared to F1 and F3 in untreated soil (Figure 4.7a). Although the percentage of F1 was low (< 2%), the concentration of Cr in this fraction was still high due to the high concentration of total Cr. It was obvious that all pyrolysis treatments without the addition of rice straw (R0-200 and R0-300) were found to cause a slight decrease in F1 and F2 fractions compared to that in the untreated soil sample. As expected, a sharp decrease occurred in the mobile fractions (F1+F2) after conversion of the untreated soil to pyrolyzed char via co-pyrolysis soil with rice straw (Figure 4.7a). Moreover, higher pyrolysis temperature also revealed lower F1 and F2 fractions. The former trend suggested that the relative unstable Cr species were immobilized by pyrolysis treatment, and the later trend indicated that the directly toxic forms of Cr (F1+F2) decreased with increasing co-pyrolysis temperature. A slight decrease in the mobile fractions (F1 and F2) was observed in the samples treated with increasing addition of rice straw at 300 ℃ (Figure 4.7b).

In summary, all the samples were found with lower Cr contents in the mobile fractions (F1+F2) as a result of pyrolysis treatment. Generally, addition of rice straw and co-pyrolysis with the soil led to further transformation of Cr to more stable forms. Co-pyrolysis temperature played a crucial role in reducing the mobilization of Cr in the samples.

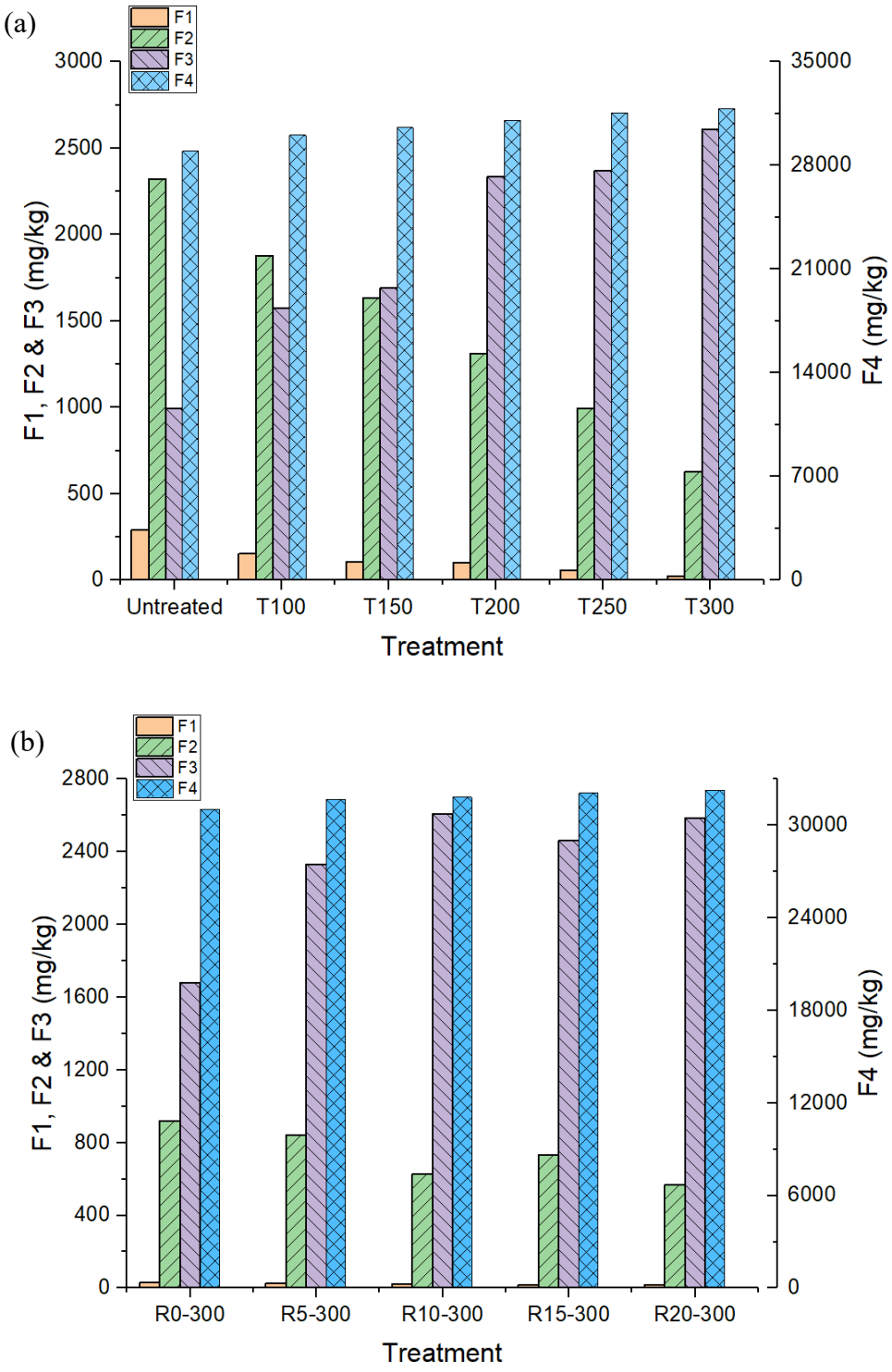


Figure 4.7 Fractions of Cr in untreated and co-pyrolyzed soil samples by BCR analysis (F1, exchangeable and acid-soluble fraction; F2, reducible fraction; F3, oxidizable fraction; F4, residual fraction), (a) different reaction time, (b) different addition ratios of rice straw at 300 ℃

4.7 Time-varying desorption kinetics

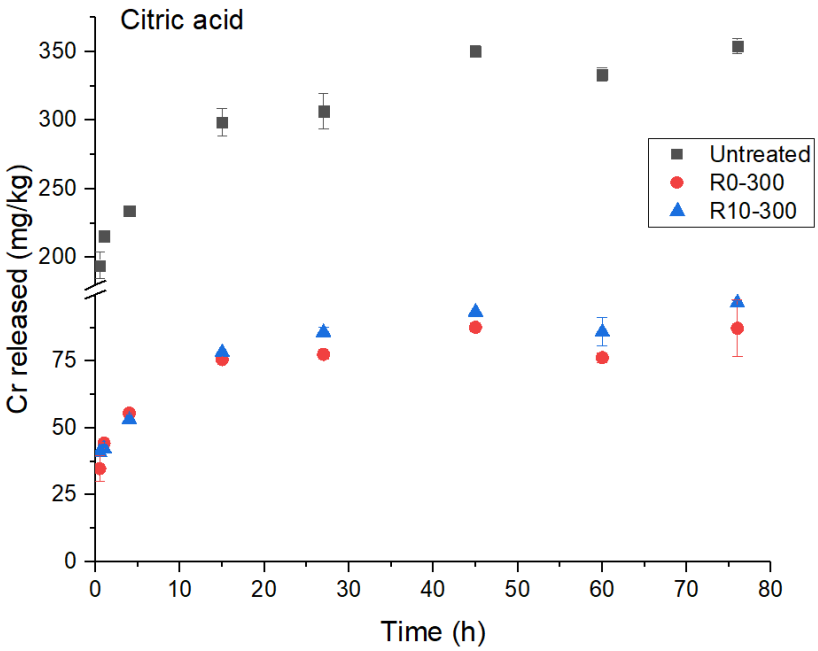
The amount of Cr released from selected representative samples using three different extractants (citric acid, nitric acid and $CaCl_2$) were presented in Figure 4.8. For all the samples, the rate of Cr desorption was fast in the first 15 h, followed by a slow approach to equilibrium. Generally, desorption amount of Cr in untreated soil after approaching equilibrium was around 21 times higher using nitric acid, 3 times higher using citric acid and 12 times higher using $CaCl_2$ than those in the treated samples (R0-300 and R10-300), respectively. Meanwhile, there were significant difference ($P<0.05$) between Cr release before and after pyrolysis treatments. Compared to R0-300, the release of Cr in R10-300 was slightly higher when extracting by citric acid and nitric acid, while it was opposite in the presence of $CaCl_2$.

Pseudo-first-order and pseudo-second-order kinetic models were then fitted to the data to elucidate the time-dependent release of Cr with time and desorption mechanism of chars before and after treatment (Table 4.6). The linear plot of $\log(q_e-q_t)$ against t presented a relationship where k1 and q_e were determined by the slope and the intercept, respectively. Another linear plot of t/q_t against t could also obtain k_2 through the slope and calculate the q_e through the intercept. The values of k_1, k_2, q_e, and correlation coefficients R^2 were shown in Table 4.6, and it was obvious that pseudo-second order kinetic model fitted better in all samples ($R^2 > 0.9$). Among the three different extractants, Cr showed the most release in untreated soil (q_e = 357.14 mg kg^{-1}) when extracted by citric acid. The q_e of the Cr from untreated soil was 270.27 mg kg^{-1} and 227.27 mg kg^{-1} using nitric acid and $CaCl_2$, respectively. When extracted by citric acid, the equilibrium amount of released Cr in all the samples were higher than those extracted by nitric acid and $CaCl_2$, especially in pyrolyzed chars, which were up to about 7 times higher than those extracted by other extractants. Qin et

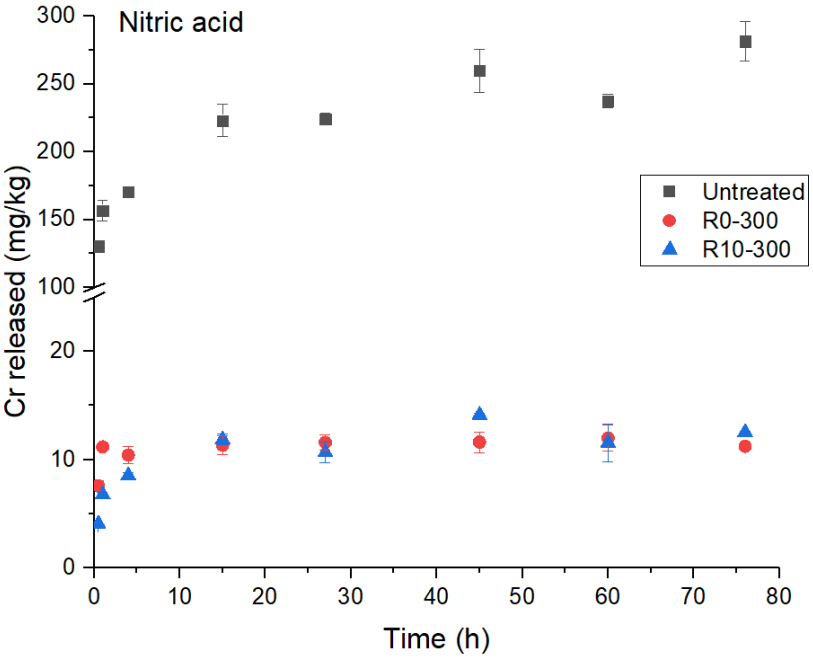
al. (2004) also found that organic acids could desorb heavy metals from the soil more efficiently than inorganic salt ($CaCl_2$). The value of k_2 increased with the pyrolysis treatment and rice straw addition, as well as in the presence of nitric acid compared to citric acid and $CaCl_2$. This indicated that pyrolyzed chars were more likely to reach equilibrium in a shorter time when extracted by nitric acid. Compared to R10-300, R0-300 had lower q_e in nitric acid and citric acid, but it had less resistance to Cr desorption due to higher k_2 in all three extractants in this study. These results suggested that Cr adsorbed in R10-300 was relatively closely, and the mobility of Cr tended to be less after this co-pyrolysis treatment.

Overall, the maximum Cr was released by the extraction of citric acid. The citric acid, as a kind of organic acids, had a strong ability to complex or chelate metals causing them to leach in greater concentrations (Townsend et al., 2004). In addition, citric acid had higher molecular weight and more functional groups, which were helpful to complex Cr (Jing et al., 2007). Therefore, citric acid had a noticeable influence on the leaching of Cr. Jean-Soro et al. (2012) investigated the column leaching of soil contaminated with Cr and Ni using citric acid and EDTA, and the results showed that citric acid leached more Cr than EDTA. Compared to untreated soil, pyrolyzed chars had lower amounts of Cr release, which was in agreement with the results of SPLP. It was also depicted that the release of Cr from R0-300 and R10-300 did not show much difference in nitric acid, but lower Cr release was found in R10-300 while using $CaCl_2$.

(a)


Citric acid
Cr released (mg/kg)
Time (h)
Untreated
R0-300
R10-300

(b)


Nitric acid
Cr released (mg/kg)
Time (h)
Untreated
R0-300
R10-300

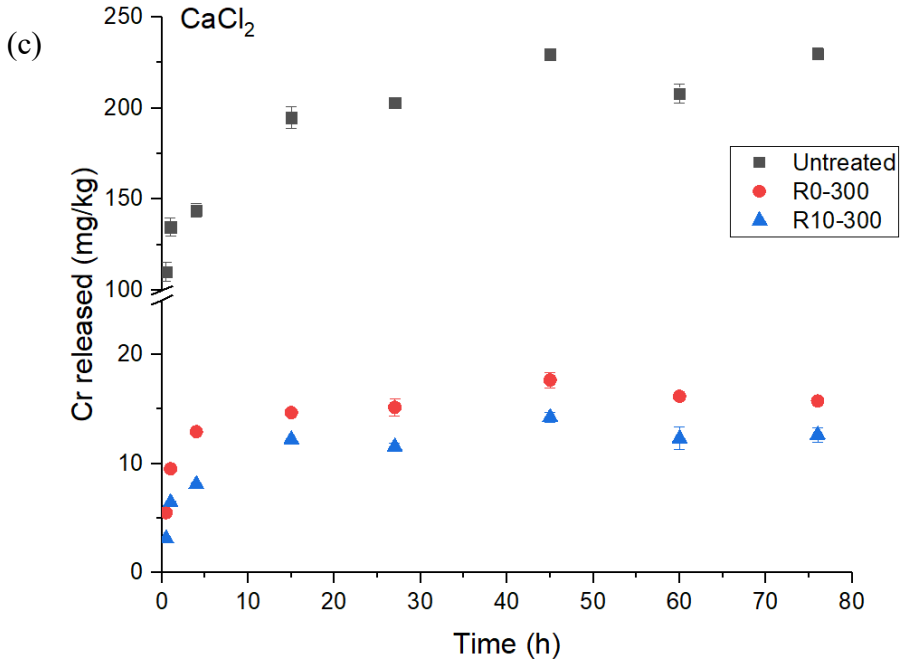


Figure 4.8 Amount of Cr released from untreated and treated samples using different extractants, (a) citric acid, (b) nitric acid, (c) $CaCl_2$ solution

Table 4.6 Pseudo-first-order and Pseudo-second-order kinetic equation parameters for the release of Cr from selected representative samples using three different extractants (nitric acid, citric acid and $CaCl_2$ solution)

Extractants	Sample ID	Pseudo-first-order			Pseudo-second-order		
		q_e	k_1	R^2	q_e	k_2	R^2
Nitric acid	Untreated	247.21	1.023	0.607	270.27	0.002	0.987
	R0-300	11.46	2.295	0.804	11.52	1.538	0.999
	R10-300	11.42	0.599	0.575	12.58	0.059	0.987
Citric acid	Untreated	312.40	1.763	0.731	357.14	0.001	0.997
	R0-300	83.98	1.040	0.938	84.75	0.008	0.992
	R10-300	85.72	0.975	0.796	95.24	0.005	0.993
$CaCl_2$	Untreated	195.61	1.362	0.700	227.27	0.003	0.995
	R0-300	15.94	0.774	0.848	16.34	0.074	0.996
	R10-300	12.62	0.550	0.846	12.99	0.056	0.993

4.8 Content of bioaccessible Cr

The results of the SBET for Cr bioaccessibility in the untreated soil and co-pyrolyzed chars were shown in Figure 4.9. Compared to untreated soil, the bioaccessibility of Cr in pyrolyzed samples decreased significantly, and it also declined approximately 70 % from 1176.6 mg kg^{-1} in raw soil sample to 358.1 mg kg^{-1} in R20-300. Considering temperature effects on bioaccessible Cr, the results were found to significantly decrease as the temperature rose from 100 ℃ to 300 ℃ . For example, the amounts of bioaccessible Cr dropped from 825.9 mg kg^{-1} (T100) to 544.8 mg kg^{-1} (R10-200) and then to 401.6 mg kg^{-1} (R10-300). On the contrary, the ratio of rice straw addition did not reflect the great differences among co-pyrolyzed chars. The data in the figure only revealed a slight decrease with the increase of rice straw addition. Therefore, the dominance of temperature on the bioaccessible Cr was suggested and the study presented some valuable data for risk assessment. Houben et al. (2013) reported that the environmental risk of soil which was inherent to heavy metals were mainly dependent on their bioaccessible contents. Although many researches were conducted to explore the bioavailability of Cr using BCR extraction, little researches were done to determine the effect of pyrolysis to the bioaccessible Cr based on SBET test.

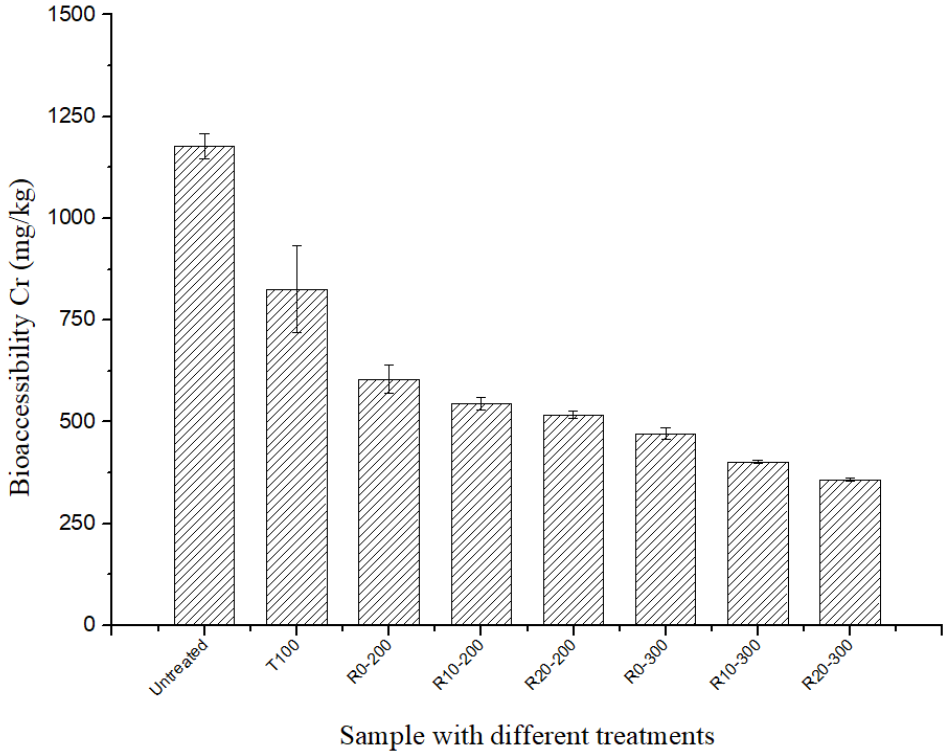


Figure 4.9 Bioavailable content of Cr in different treated samples by a SBET method

4.9 Characterization of pyrolyzed chars (SEM, XRD and FTIR)

The SEM results were shown below (Figure 4.10, Figure 4.11, Figure 4.12 and Figure 4.13) for comparing the differences of the morphology between raw soil sample and co-pyrolyzed samples. The SEM images were taken at 500X, 2000X, 5000X and 10000 X magnification for further exploring the surface morphology and pore structure. It was obvious that the surface morphology of soil sample before (Figure 4.10) and after pyrolysis treatment (Figure 4.11) were different. Upon pyrolysis treatments, surface coatings were observed on the soil sample. The SEM images also revealed less porous structure in R0-100 comparing to untreated soil, which may be because pores were blocked by tar or surface coatings. As the temperature rose from 200 ℃ (Figure 4.13) to 300 ℃ (Figure 4.12), the surface morphology and porous structure were gradually developed. The untreated soil

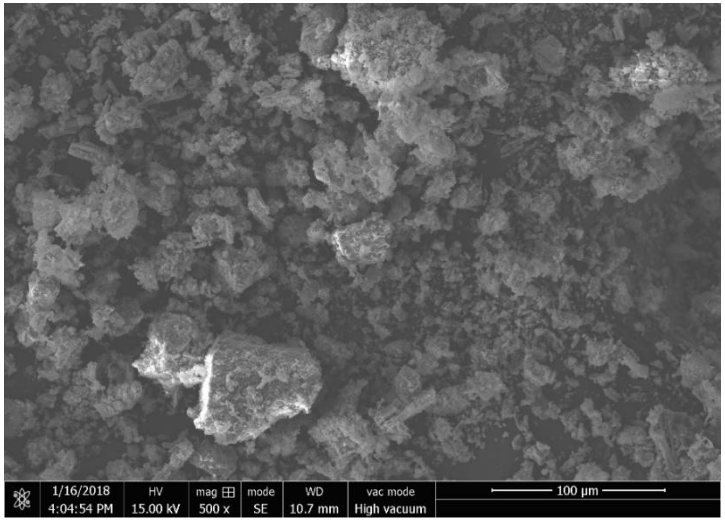
material had relatively smooth surface, while the rice straw had rougher surface and more pore structure. Therefore, with the addition of rice straw during pyrolysis process, more surface coatings and bigger pore diameter were found in the Figure 4.12 and Figure 4.13 compared to that in the Figure 4.10 and Figure 4.11. These phenomena were also indicated by the data of BET test whose pore diameter increased with elevated temperature and rice straw addition. Moreover, rice straw addition contributed to more surface coatings due to the partially charred biomass and closely bounded biomass-soil matrix (see Figure 4.11 and Figure 4.12). Comparing Figure 4.12c and Figure 4.13c, fiber structure of rice straw pyrolysis at 200 ℃ was clearer, while more coatings were closely combined with rice straw at 300 ℃ .

XRD diffractions patterns of raw soil sample and its co-pyrolyzed chars (R0-300, R10-300) were depicted in Figure 4.14. Based on the XRD intensity of different crystalline materials, it was obvious that all three samples contain large amounts of calcite ($CaCO_3$). Tang et al. (2008) reported that during the pyrolysis process, the organic matter and $CaCO_3$ decomposed and then the peak decreased. Compared to pyrolyzed samples (R0-300, R10-300), the peak of calcite weakened after pyrolysis treatment at 300 ℃ . The decomposition of $CaCO_3$ generated free CaO during pyrolysis process which could immobilize Cr by forming a more stable complex (Hu et al., 2013). This was in agreement with previous results that Cr was not prone to leaching after pyrolysis treatment. Quartz (SiO_2) and chromium oxide (Cr_2O_3) were also observed as main components in all the samples. For untreated soil, a peak around $2\theta = 27°$ was distinct and disappeared after pyrolysis treatments, which was associated with CrOOH. This disappeared peak may be because CrOOH transformed to Cr_2O_3 after pyrolysis treatments. Li et al., (2008) and Liang et al. (2014) also reported CrOOH was usually used to obtain Cr_2O_3 through thermal decomposition. The results of

XRD analyses therefore indicated that the Cr(III) was the main form, and no Cr(VI)-containing crystalline phases were found by XRD, which may be limited by the low Cr(VI) content compared to high amount of Cr(III). Similar results were found by Zhou et al. (2018) who pyrolyzed tannery sludge during low temperature, and XRD results showed that no Cr(VI)-containing components were found by XRD although their tannery sludge had a high concentration of total Cr. In addition, no obvious mineral transform was found during the process of pyrolysis treatment at 300℃ .

The FTIR spectroscopic study of the raw sample and produced chars were shown in Figure 4.15. It was obvious that FTIR spectra of untreated soil and its co-pyrolyzed chars were similar, which indicated that the pyrolysis treatment and rice straw addition during pyrolysis treatment did not contribute to noticeable functional groups changes. This phenomenon may be due to that soil sample in this study contained the main functional groups present in rice straw, and these functional groups did not disappear under 300 ℃ pyrolysis treatments. Similar results were reported by Huang et al. (2017) who also found no significant functional group changes present in biochar from different feedstocks (sewage sludge, sewage sludge-rice straw, and sewage sludge-sawdust). The intensity of the peak around 3400 cm^{-1} slightly decreased in R10-300 compared to untreated soil, indicating that a part of hydroxyl groups was decomposed after pyrolysis with rice straw at 300 ℃ (Leng et al., 2015). Devi and Saroha (2013) reported the presence of peak at 3393-3423 cm^{-1} was due to the water molecule absorption as a result of hydroxyl group stretching and adsorbed water. The peak around 3141 cm^{-1} was thought to be amides and amines, and the peaks between 1300 and 1797 cm^{-1} could further confirm the presence of amides (Pokorna et al., 2009). Moreover, the absorption at 1026 cm^{-1} could be associated with C-O-C symmetric stretching vibrations or anti-symmetrical Si-O-Si stretching due to the presence of quartz in the samples

(Hamed, 2014). The peaks between 600 and 800 cm^{-1} were due to the presence of aromatic and heteroaromatic compounds, which would provide π-electron to strongly bond heavy metal cations (Harvey et al., 2011).



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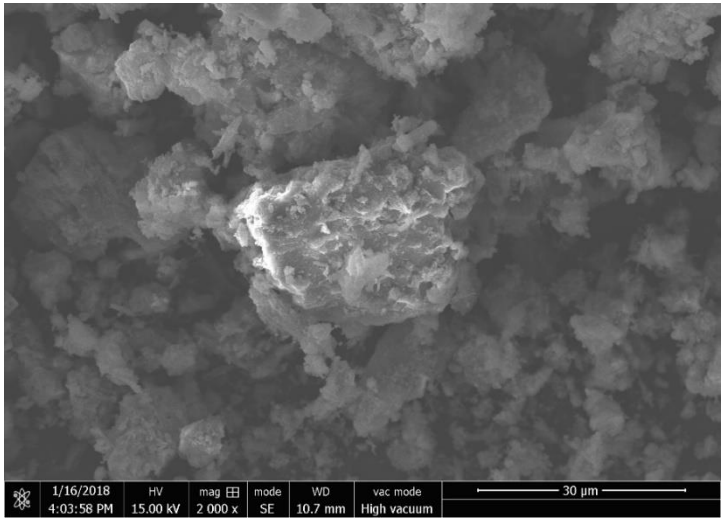

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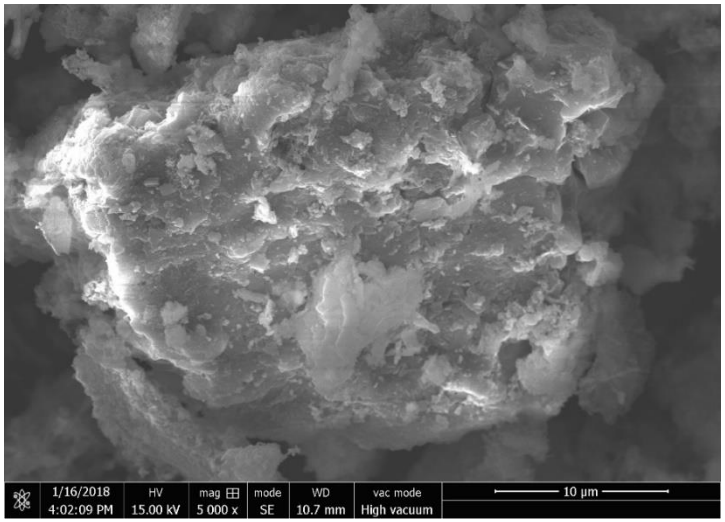

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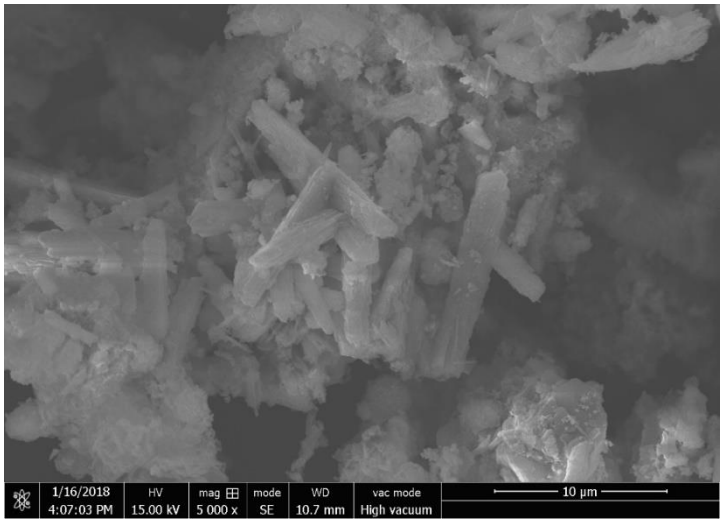

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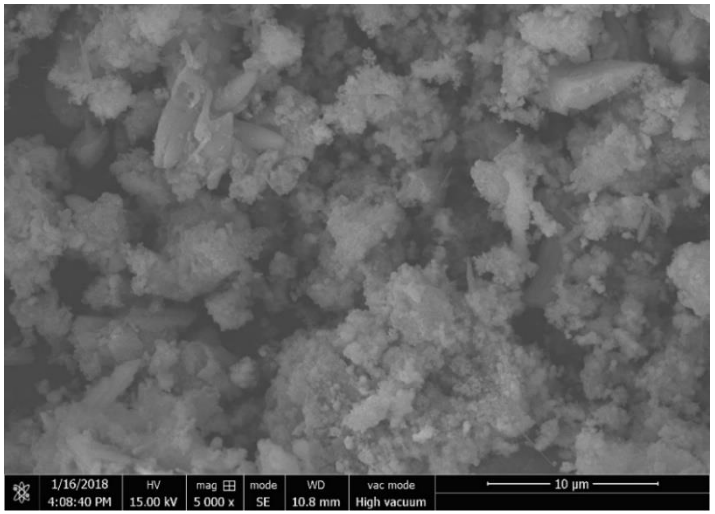

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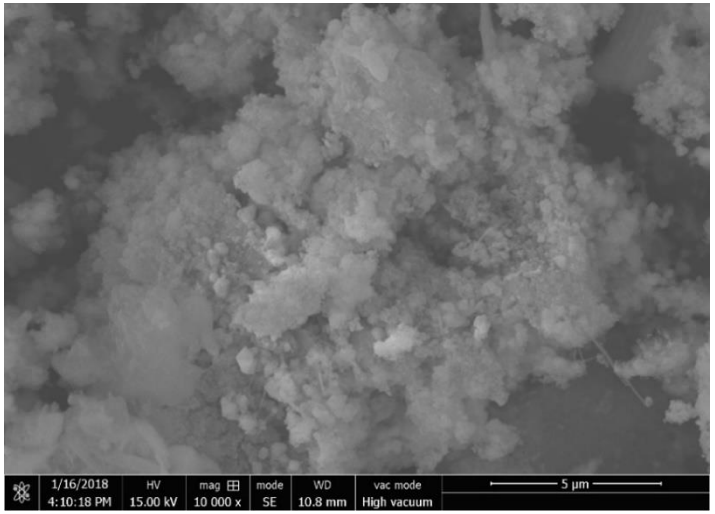
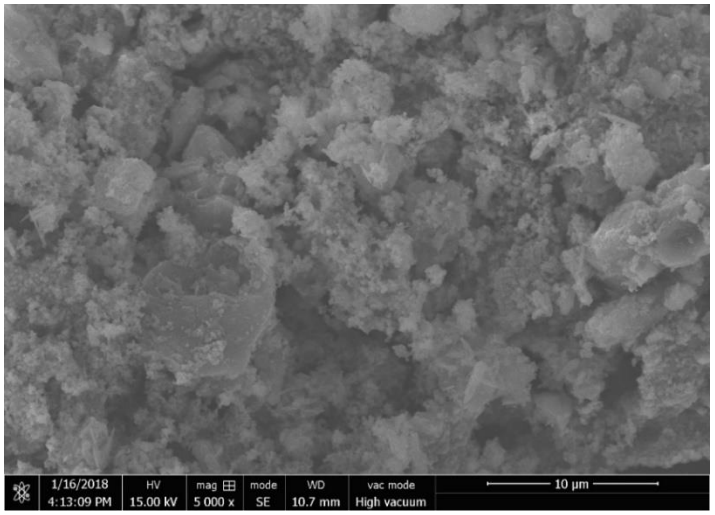


(f) 10000X



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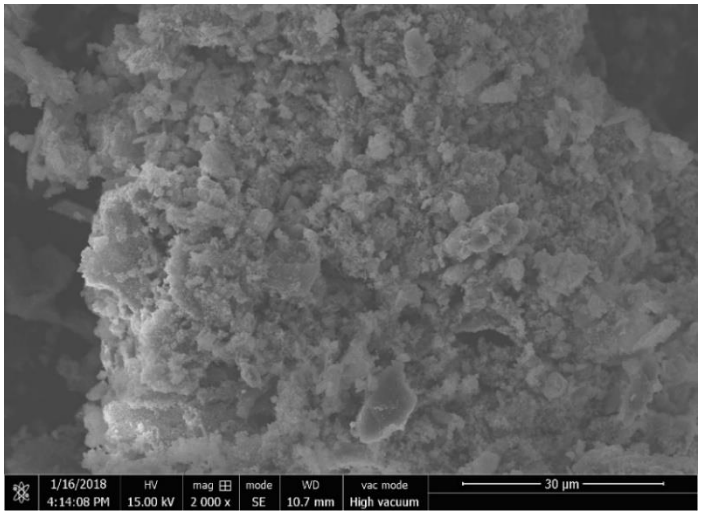
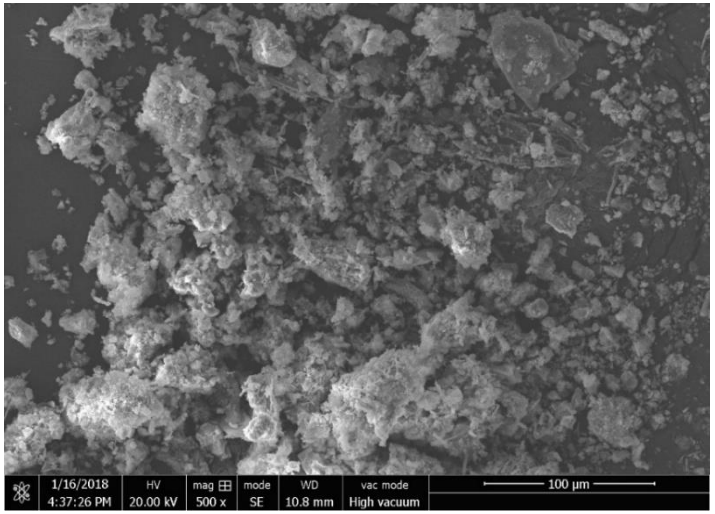


(h) 5000X

Figure 4.10 SEM of untreated soil



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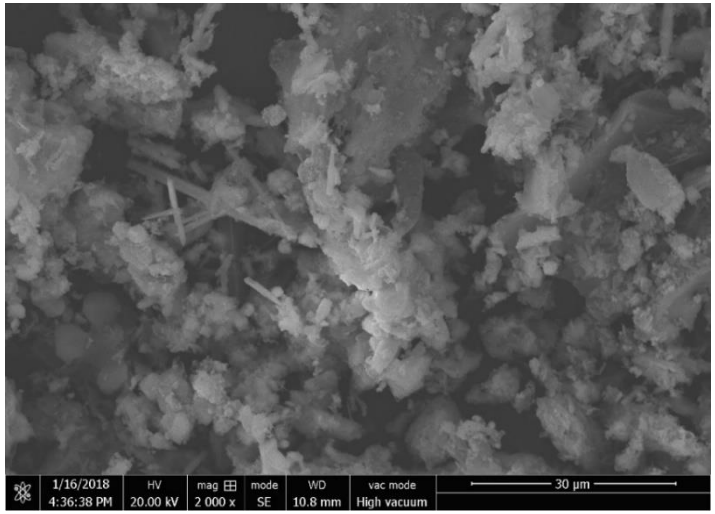

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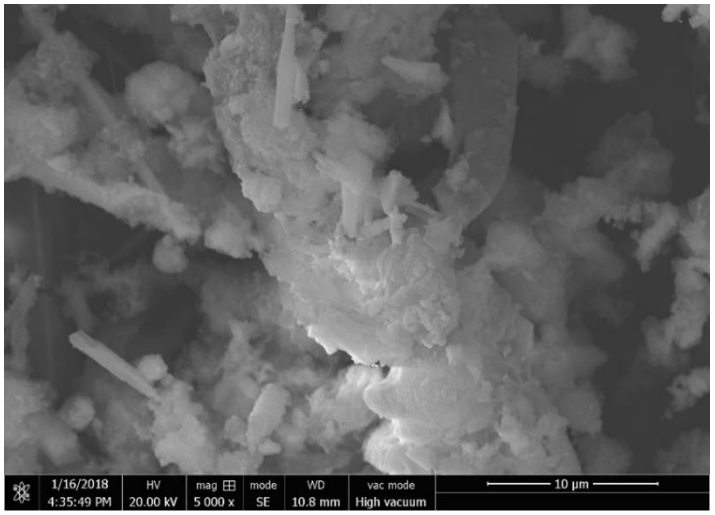

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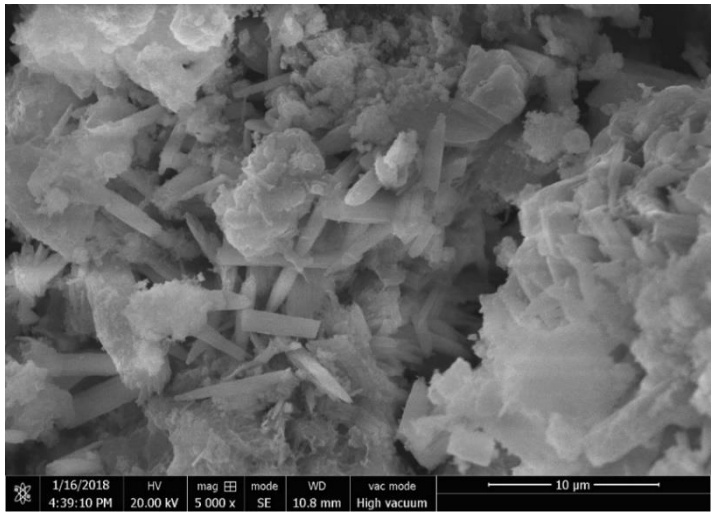

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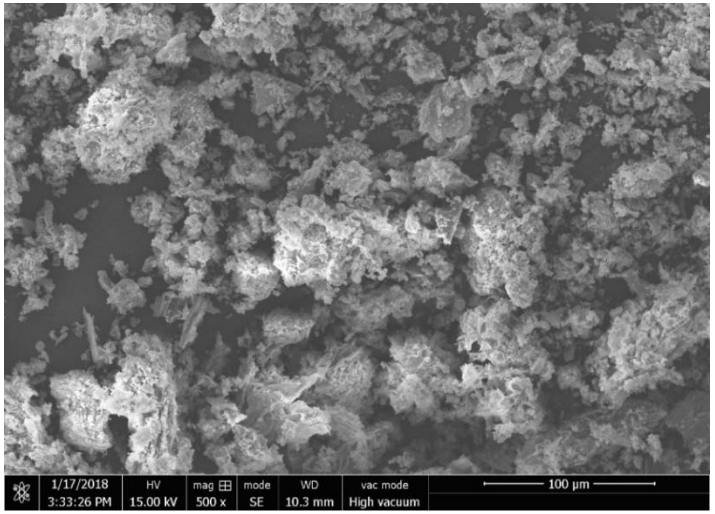
Figure 4.11 SEM of soil sample R0-300



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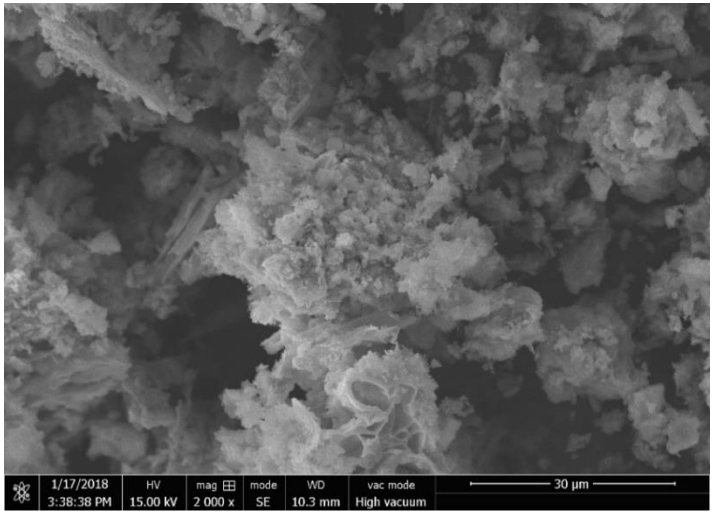

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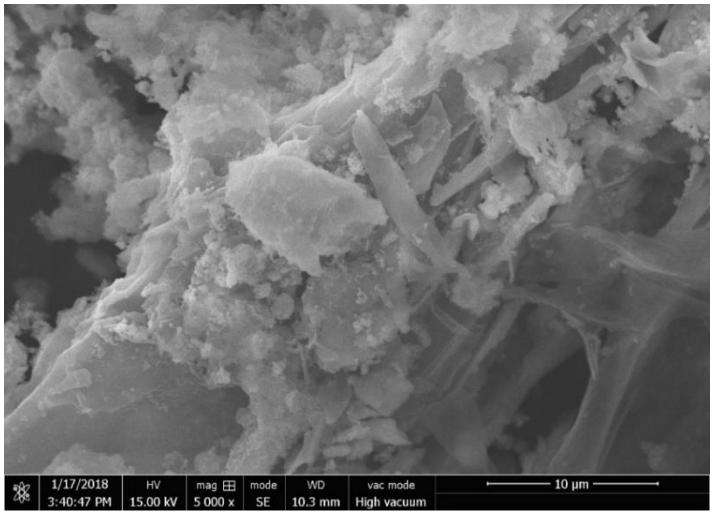

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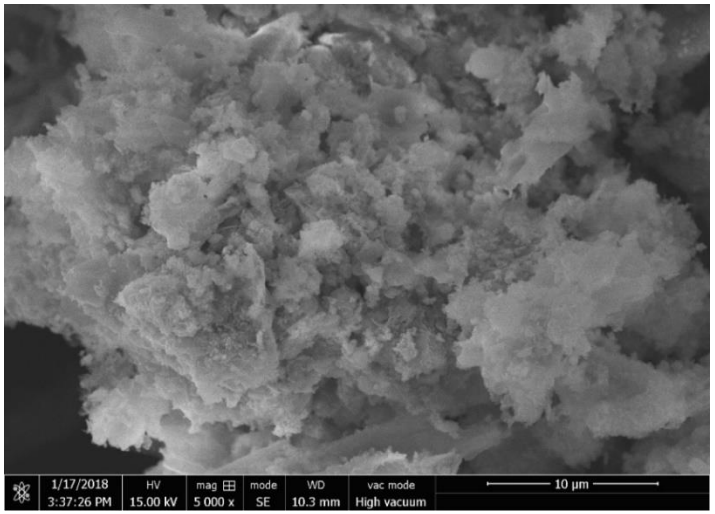
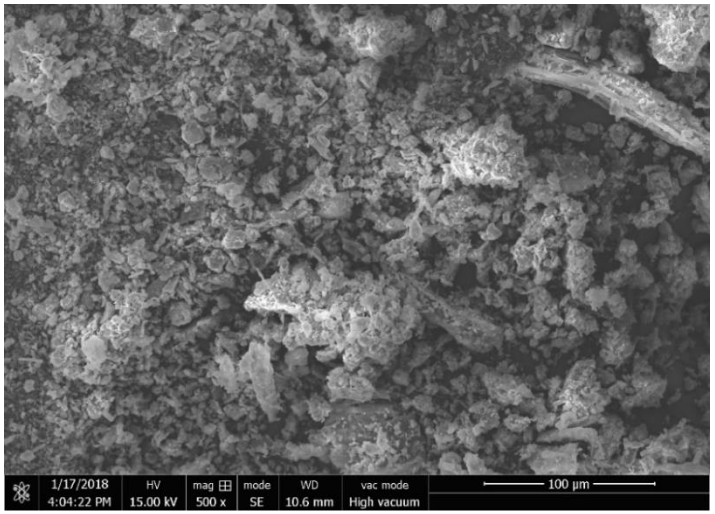


(d) 5000X

Figure 4.12 SEM of soil sample R20-300



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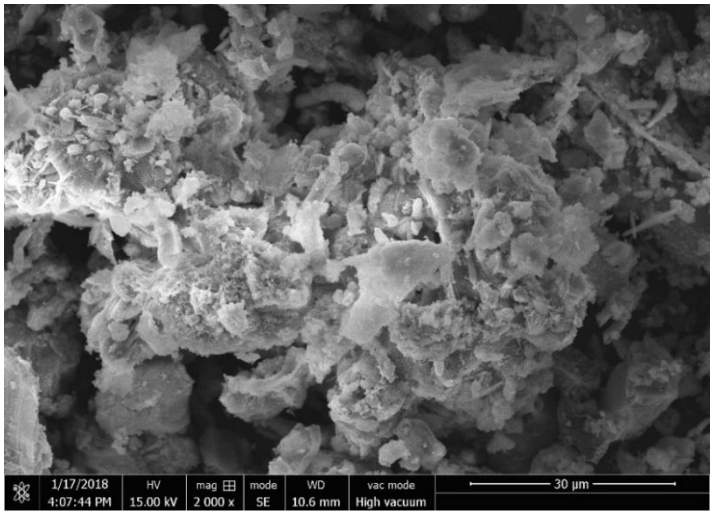

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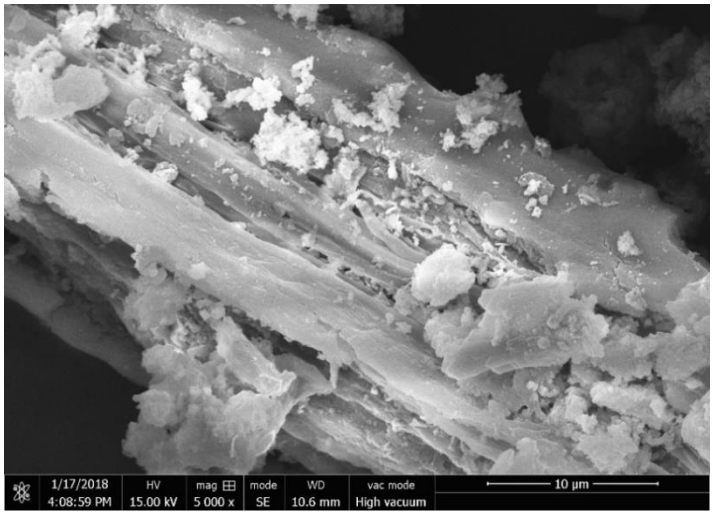

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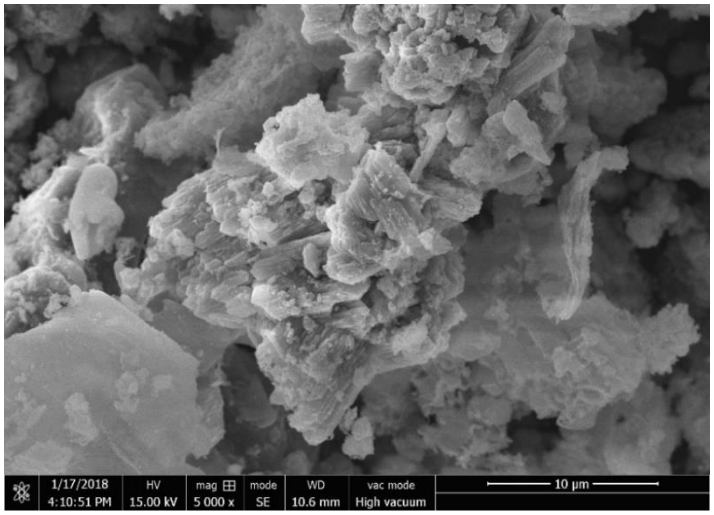

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Figure 4.13 SEM of soil sample R20-200

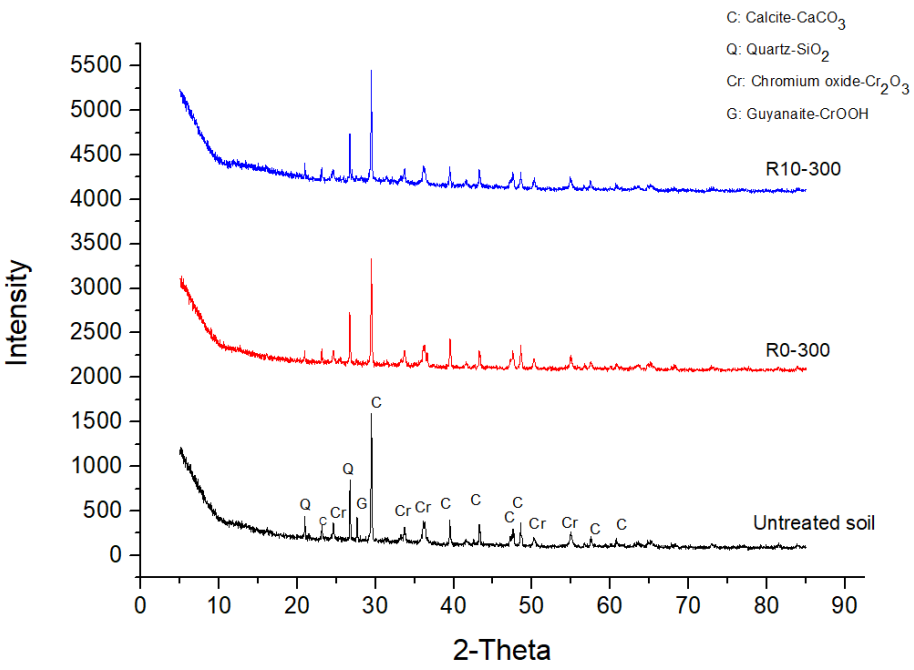

Figure 4.14 XRD spectra of untreated soil and selected pyrolyzed samples (R0-300 and R10-300)

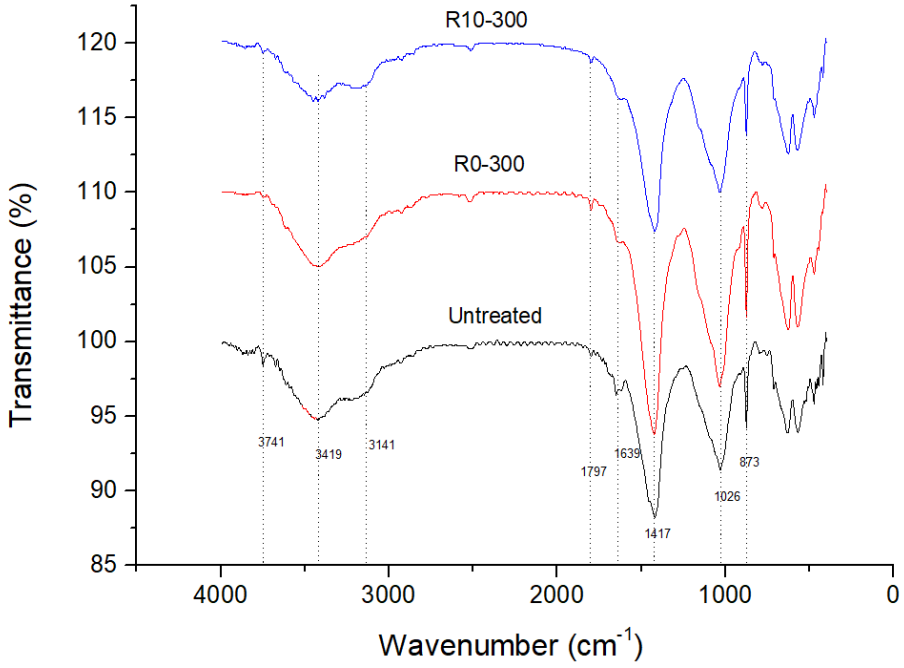

Figure 4.15 FTIR spectra of untreated soil and selected pyrolyzed samples (R0-300 and R10-300)

4.10 Potential benefits and challenges of applying the proposed co-pyrolysis technique commercially

The untreated soil sample in this study contained a high concentration of total Cr, and its total content of Cr(VI) was about 1018 times higher than the limit of 0.4 mg kg^{-1} recommended by Canadian Soil Quality Guidelines (CCME, 1999). The co-pyrolysis treatment in this study could efficiently decrease the leachable Cr and Cr(VI) contents, but it still exists several important factors restricting the industrial application of this co-pyrolysis technique. These factors include economic benefits, long-term effectiveness and environmental considerations.

Considering the economic aspects, cost and time required in the treatment determine the success of this co-pyrolysis technique when applied in the field remediation. Effectiveness for highly Cr contaminated soil is difficult to achieve using techniques such as isolation, phytoremediation or bioremediation, but co-pyrolysis could quickly and efficiently immobilize Cr. However, to proceed co-pyrolysis treatment, excavating the soil is inevitable, and excavation could be very expensive for large amount of soil. Therefore, co-pyrolysis treatment requires a relative high cost due to the high energy consumption compared to economical treatments such as natural bioremediation or phytoremediation. Nevertheless, those economical treatments require long-time periods to completely remediate the soil. In this study, co-pyrolysis could efficiently decrease Cr leaching and Cr(VI) contents at relative low temperatures ($\leqslant$ 300 °C) in short treatment durations, which lowers energy consumption and cost and makes economic benefits achievable.

Compared to bioremediation and phytoextraction, co-pyrolysis does not need to adjust soil conditions for microorganisms or plants when applying to highly contaminated soil.

Although the co-pyrolysis treatment in this study could not permanently remove Cr from soil, Cr was immobilized in the soil. In order to assess the potential risk and long-term stability, the time-varying desorption tests, BCR sequential extraction and total Cr(VI) contents were conducted. The results in this study showed that co-pyrolysis could effectively reduce leachable Cr and transform Cr(VI) to Cr(III). Considering the chemistry of Cr, the reduction of Cr(VI) to Cr(III) is easier compared to the oxidation of Cr(III) to Cr(VI), and the oxidation conditions are limited by manganese oxides, water-soluble Cr, pH or ionic strength. In this study, the total Cr(VI) was decreased up to 86%, and it would be difficult to oxidize Cr(III) due to the unavailability of mobile Cr(III). Hence, this co-pyrolysis could be effective for long term, but regular monitoring system is still required to ensure that the immobilization conditions are sustained.

Unlike chemical remediation, co-pyrolysis would not generate secondary pollution in the site. The gas generated during the co-pyrolysis process could be collected and then used to generate heat or electricity. The oil generated could also be refined for engine fuels, chemicals, adhesives or other products. Consequently, the co-pyrolysis treatment appears to be a promising and acceptable for industrial application for the remediation of contaminated soil with high concentrations of Cr.

Chapter 5 Conclusions

5.1 Research summary

Although several studies have reported the effects of co-pyrolysis of sewage sludge and biomass on the immobilization of heavy metals, only a few researches studied the application of co-pyrolysis and impacts of co-pyrolysis Cr-contaminated soil with rice straw under temperature100-300 °C on Cr immobilization. The following conclusions have been obtained:

(1) The physicochemical properties of untreated soil and co-pyrolyzed chars under different conditions were analyzed. The LOI value was increased with the elevated temperature and rice straw addition, while no obvious influence was observed on longer reaction time. The soil collected in this study was alkaline soil, and its pH increased after pyrolysis soil or co-pyrolysis Cr contaminated soil with rice straw. Increasing pH was helpful to decrease the leachable Cr and Cr(VI) content. The volatilization of organic matter during co-pyrolysis treatment was also beneficial to Cr(VI) reduction.

(2) As expected, pyrolysis of Cr-contaminated soil could immobilize Cr, and co-pyrolysis of rice straw and Cr-contaminated soil could further reduce the toxic form of Cr based on the results of less Cr leaching (reduced up to 95 %), lower Cr (VI) concentrations (decreased up to 86 %) and less mobile Cr species (F1 and F2) compared to untreated soil. With the rising pyrolysis temperature, leachable Cr and total Cr(VI) concentration were decreased up to 81 % and 73 %, respectively. The fractions of Cr were also transformed from the mobile forms (F1 and F2) to more stable forms (F3 and F4). Similarly, increasing amount of rice straw during the pyrolysis process was able to decrease the content of leachable Cr (up to 47%) and transform Cr to more stable forms under 300 ℃ pyrolysis treatment, but had no influence on reducing the leachable Cr when conducted at 200 ℃ . However, addition

ratio of rice straw played an important role on transforming Cr(VI) to Cr(III), which could effectively reduce Cr(VI) (up to 52%) with increasing addition of rice straw. Overall, the optimal co-pyrolysis treatment conditions observed in this study were adding 20 % of rice straw and using 300 ℃ , which could reach the lowest leachable Cr and total content of Cr (VI). However, reaction time did not show an obvious impact on reducing the toxicity of Cr.

(3) Time-varying desorption experiments were conducted in this study, and the results showed that our co-pyrolysis treatment could efficiently reduce the Cr release by three different extractants (citric acid, nitric acid and $CaCl_2$). Citric acid as an organic acid commonly present in the rhizosphere soil could extract more bioaccessible Cr than nitric acid and $CaCl_2$. Compared to R0-300, R10-300 showed lower Cr desorption when extracted by $CaCl_2$, but R0-300 released less Cr in citric acid. Meanwhile, it was found that the pseudo-second order kinetic model fitted better in Cr desorption ($R^2 > 0.9$). To further assess the bioaccessibility of Cr adsorbed in gastrointestinal system, SBET test was conducted and results showed that up to 70% of bioaccessible Cr decreased after co-pyrolysis treatment.

5.2 Limitations and future research

In this study, co-pyrolysis Cr contaminated soil with rice straw under temperature 100-300 °C was found to effectively immobilize Cr with low cost. This treatment is of great advantages over others due to its cost-effectiveness and applicability to large scale. However, the effects of this co-pyrolysis treatment on the reduction of Cr (VI) and Cr leaching were limited. Different kinds of biomass could be applied and compared for better reducing the toxicity of Cr and temperature range could be expanded to support enough energy to modify Cr species and mineral components. In the future, more mechanisms of reducing the toxicity of Cr should be investigated. The gas generated during the co-pyrolysis treatment should be

collected and examined to better evaluate the effects of volatile gas on reduce the toxicity of Cr. The impacts of organic matter on Cr distribution could be explored as well. The spatial association between Cr and soil mineral using synchrotron-based technique could be conducted to better understand the distribution of Cr (III) and Cr (VI).

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